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AFRPL-TR-67-158

THE DEVELOPMENT AND EVALUATION OF A HYDROCARBON BINDER FOR HIGH ENERGY SOLID PROPELLANTS (U)

By

D. E. Johnson, R. H. Quacchia, and A. J. DiMilo
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Solid Propellant Operations
Sacramento, California

April, 1967

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Air Force Rocket Propulsion Laboratory
Research and Technology Operations
Edwards, California
Air Force Systems Command
United States Air Force

1030

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(U) THE DEVELOPMENT AND EVALUATION OF A HYDROCARBON BINDER FOR HIGH ENERGY SOLID PROPELLANTS

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FOREWORD (U)

(U) This technical report was prepared under Contract No. AF 04(611)-11419 as partial fulfillment of the requirements of Project 3418 of the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Edwards, California. This final report covers all the work done on Phases I, II, and III under the above cited contract. Also included is the work done to-date on Phase IV, but work is continuing on this phase and on Phase V. The work reported was done in the Advanced Propellants Department of the Aerojet-General Corporation, Sacramento, California. This report was designated Aerojet-General Report 1030-81F and covers the results of work done during the interval 14 March 1966 to 13 March 1967. The project was a follow-on to the project completed under Contract AF 04(611)-10386, the results of which are reported in Report No. AFRPL-TR-66-40. This project was monitored by Mr. Robert Corley.

(U) This report contains classified information extracted from the following documents: AFRPL-TR-66-159 and -257 and -67-5 (Quarterly Reports 1-3 of this contract), References 14, 15, and 16.

(U) Acknowledgement is made to the following persons who have contributed materially to the work performed during this period: R. J. Smith, Senior Chemist; J. L. Humphreys, Associate Chemist; A. H. Swift, Chemist; R. J. Farris, Physicist; B. B. White, Supervisor Mechanical Properties Laboratories; F. H. Davidson, Liaison Engineer Mechanical Properties Laboratories; and at The General Tire and Rubber Company, to: R. G. Chase, Technical Assistant to the Technical Coordinator, Research and Development.

(U) This technical report has been reviewed and is approved.

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ABSTRACT (U)

(U) The investigation and characterization of the saturated hydrocarbon binder developed under Contract AF 04(611)-10386 for use in solid rocket propellant were continued. The molecular weight and functionality distributions were determined for the saturated hydrocarbon prepolymer and found to be independent of each other. Analytical data were obtained for saturated and unsaturated prepolymers with hydroxy or carboxy terminal groups.

(U) While NH_4ClO_4 and Al were compatible with the isocyanate curing agents, many plasticizers were not. Of the plasticizers, the hydrocarbon oils were most compatible. The difficulties with the plasticizers were the presence of impurities and an effect (not the result of impurities) on the cure of binders. Binders were made from the Telagen S prepolymers and characterized by uniaxial tensile behavior at 77°F, stress relaxation at 77° and 150°F, compression after swelling in toluene, gel and sol fractions, and Mooney-Rivlin constants. Linear relations were demonstrated between the gel fraction, the Mooney-Rivlin C_1 constant, the crosslink density, and the logarithm of the initial uniaxial tensile modulus and of the maximum tensile stress. These data obtained for binders containing a variety of plasticizers seemed to indicate that no plasticizing action exists in these binders. Swelling studies in a large number of solvents indicated a CED value of about 80 for the binder. Two new curing agents, RTDI (an isocyanate) and C-100 (an aziridine), were inferior to the currently used CTI-HDI combination. Propellant studies led to a candidate formulation which differed slightly from the original workhorse propellant. This propellant showed good aging in screening tests, but continued to have disappointing properties at low temperature. Two 125-lb batches of the propellant were prepared, cast, cured, and placed in long-range aging.

(C) The pressure exponent for burning rate was 0.7 for these propellants (88 wt% solids). The relative viscosity of NH_4ClO_4-Oronite 6 slurries was at a minimum for an oxidizer blend of 35.80%, 32.10% and 32.10% by weight of particles averaging 6, 148, and 419μ, respectively. This blend was used to prepare a high solids loaded propellant with 79% NH_4ClO_4, 12% aluminum, and 9% Telagen S binder at 60-lb scale. Small motors of this propellant, which had a burning rate-pressure exponent of about 0.8, were fired. The specific impulse at standard conditions for large motors was 250 lbf-sec/lbm. The mechanical behavior of this propellant was extensively characterized.

(U) The compatibility of the prepolymer and model compounds with beryllium, LMH-1 and LMH-2 was determined. The most difficulty involved LMH-1 and a model isocyanate. Propellants were made with the Be and LMH-2, but preparation of propellants with LMH-1 required pretreatment of the LMH-1 and catalysis of the isocyanate reaction to maintain ambient curing conditions.

ABSTRACT (CONT)

(C) Compatibility studies were extended to include epoxide and aziridine curing agents as well as isocyanates and the oxidizers HAP and HDP. Carboxy, hydroxy and olefinic functional groups were compatible with HAP. Isocyanate was the only curing agent which appeared practical in the HAP system. Both HAP and HDP accelerate the isocyanate-alcohol reaction. In the case of HAP, the use of the amine DAM slowed the isocyanate reaction although it was still much faster than in the absence of the HAP. Both of the oxidizers, physically adsorbed urethane, but with HDP, some chemical degradation was also observed. A series of hydroxyl-amine-HAP complexes were made, identified, and studied.

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FIGURES (Cont)

GLOSSARY OF TERMS (U)

ADN	Adiponitrile
Aerosol TR	Bis(tridecyl)sulfosuccinate, product of the American Cyanamid Company
Ansul Ether 181	Tetraethylene glycol dimethyl ether
Arneel OD	Oleylnitrile, product of the Armour and Company
Antioxidant 2246	2,2'-Dihydroxy-4,4'-dimethyl-6,6'-di-t-butyldiphenylmethane, product of the Union Carbide Company
a_T	WLF shift factor
BDNPA	Bis(dinitropropyl)acetal
BDNPF	Bis(dinitropropyl)formal
Be	Beryllium
BISA	2-Ethylaziridine adduct of sebacic acid (HX-760), product of the Minnesota Mining and Manufacturing Company
b.p.	Boiling point
Butarez CTL	Carboxy-terminated polybutadiene, product of the Phillip's Petroleum Company
C-1	N,N-di-(2-cyanoethyl)-2,3-dihydroxypropylamine
C_1 and C_2	Mooney-Rivlin constants
C-100	1,3,5-trimethyl-2,4,6-tri[3-(2-methylaziridinyl-1) butyroxymethyl]benzene, product of the American Cyanamid Company
Carbowax 6000 Carbowax 20M	Solid poly(ethylene glycol), product of the Union Carbide Company
Carwinate 136T	Bitolylene diisocyanate, product of the Upjohn Company
CED	Cohesive energy density
Citroflex A2	Triethyl acetylcitrate, product of C. Pfizer Co., Inc.
CoAA	Cobalt acetylacetonate
CTI	Triisocyanate, proprietary item of the Aerojet-General Corporation

GLOSSARY OF TERMS (CONT)

DAM	N,N-Diallylmelamine (Confidential)
DC 705	Silicone oil, product of Dow Chemical Company
DEA	Diethanolamine
Diatoport S	Diatomaceous earth used for chromatograph support, product of F & Scientific Corporation
DOS	Dioctyl sebacate, product of the Deecy Products Division, Reichold Chemicals, Inc.
DOZ	Dioctyl azelate
Dri - Na	Sodium-lead alloy, product of the J. T. Baker Chemical Company
DTA	Differential thermal analysis
E_0	Initial uniaxial modulus
FeAA	Ferric acetylacetonate
GLC	Gas-liquid chromatography
GTRO	Glycerol triricinoleate
HAA	Acetylacetone
HAP	Hydroxylammonium perchlorate (Confidential)
HAP-X	Hydroxylammonium perchlorate monohydroxylamine complex (Confidential)
HAP-2X	Hydroxylammonium perchlorate dihydroxylamine complex (Confidential)
HC-434	Carboxy-terminated polybutadiene, product of Thiokol Chemical Corporation
HDI	Hexamethylene diisocyanate
HDP	Hydrazinium diperchlorate (Confidential)
Hycar CTB	Carboxy-terminated polybutadiene, product of B. F. Goodrich Chemical Company

GLOSSARY OF TERMS (CONT)

IDP	Isodecyl pelargonate, product of Emery Industries, Inc.
IR	Infrared
I_s	Specific impulse
Light Circo Oil	General purpose naphthenic type softener for neoprene and natural rubber, product of the Sun Oil Co.
LMH-1	Aluminum hydride (Confidential)
LMH-2	Beryllium hydride (Confidential)
MAPO	Tris-(2-methylaziridinyl-1)phosphine oxide, product of the Interchemical Company
mm/gm	Millimoles per gram
MS	Molecular sieve, 4A, product of the Linde Company
MW	Molecular weight
Macconate H-12	Bis(4-isocyanatocyclohexyl)methane, product of the Allied Chemical Corporation
NEMNC	2-Nitratoethyl N-nitro-N-methylcarbamate
NFPA	2,3-Bis(difluoramino)propyl acrylate (Confidential)
Niax D-22	Dibutyltin dilaurate, product of the Union Carbide Company
NMR	Nuclear magnetic resonance spectroscopy
NP	Nitronium perchlorate (Confidential)
Nujol	Mineral oil (registered trade name), product of Plough, Inc.
Oronite 6	Liquid polyisobutylene, product of the California Chemical Company
psi	Pounds per square inch
R-TDI	Reduced toluene diisocyanate, product of Union Carbide Company

GLOSSARY OF TERMS (CONT)

S-141	Octyl diphenyl phosphate, product of the Monsanto Chemical Company
T-12	Dibutyltin dilaurate, product of the Metal & Thermite Corporation
T-20	Sulfur-tin organic compound of unknown structure, product of the Metal & Thermite Corporation
Telagen CT	Carboxy-terminated polybutadiene, product of The General Tire and Rubber Company
Telagen S	Functionally-terminated hydrogenated polybutadiene, product of The General Tire and Rubber Company
TDI	2,4-Toluene diisocyanate
T_G	Glass transition temperature
t_m	Time to maximum stress
TMETN	Trimethylolethane trinitrate, 1,1,1-tri(nitratomethyl)-ethane
T_s	WLF reference Temperature
TVOPA	1,2,3-Tris[1,2-bis(difluoramino)ethoxy]propane (Confidential)
v_2	Gel fraction
VPO	Vapor phase osmometer
X_D	Crosslink density, moles of crosslinks per gram
ϵ_b	Uniaxial strain at break
ϵ_m	Maximum uniaxial strain
η	Viscosity, specifically for slurries
η_o	Viscosity, specifically for liquids
η_r	Relative viscosity, ratio of η to η_o
μ	Micron

GLOSSARY OF TERMS (CONT)

ν_e/V	Crosslink density, moles of chain per cc.
σ_b	Uniaxial break stress
σ_m	Uniaxial maximum stress
τ	Relaxation time; time for stress to fall to 1/e of initial value
ϕ	Volume fraction
ϕ_f	Maximum volume fraction
χ	Flory-Huggins interaction parameter

THE DEVELOPMENT AND EVALUATION OF A HYDROCARBON BINDER FOR HIGH ENERGY SOLID PROPELLANTS (U)

I. INTRODUCTION (U)

(U) This is the Final Technical Report submitted in partial fulfillment of the requirements of Contract AF 04(611)-11419. The report covers all the work on Phases I, II, and III, and the work to date on Phase IV, which is continuing. The work was performed in the period 14 March 1966 to 13 March 1967.

II. OBJECTIVE (U)

(U) The objective of this program was to further develop and evaluate a solid propellant binder system specifically to meet the most rigid demands of advanced, high performance solid rocket motors. The solid propellant binder system consisted of an isocyanate-cured, saturated hydrocarbon prepolymer developed and evaluated under Contract AF 04(611)-10386. Further development and evaluation involved propellant optimization, maximizing solids loading, adaptation to advanced oxidizers and fuels, and study of the environmental stability of the propellant.

III. SUMMARY (U)

(U) The following is a summary of the results of the work of the past year.

(U) A. Two batches (23 and 46 lb) of secondary-hydroxy terminated Telagen S and a batch of carboxy terminated Telagen S were prepared by The General Tire and Rubber Company for use by this program. In addition, the corresponding unsaturated prepolymer of one of the hydroxy terminated polymers and an unsaturated carboxy-terminated polymer were made available to the program. Analytical data on all of these prepolymers were accumulated.

(U) B. Molecular weight and functionality distributions on one prepolymer (Lot 8507-I-47.1) were narrow, 92% between 1430 and 1678 molecular weight and 1.5 and 1.7 functionality. There was no change of functionality with molecular weight as frequently shown by unsaturated prepolymers. This may indicate that unsaturated prepolymers are subject to oxidative crosslinking during the distribution determination by gel chromatography or solvent precipitation.

(U) C. Functionality by molecular weight to equivalent weight ratio continued to be lower than that obtained from the mechanical behavior of cured polymers. The conclusion was that functionality from polymer crosslink densities (termed effective functionality) was more reliable. Effective functionality differed from the expected functionality (molecular weight to equivalent weight ratio) because low molecular weight, possibly non-functional components, were lowering the observed molecular weights. In general, the effective functionalities of the Telagen S prepolymers were in the range 1.88 to 1.90.

(U) D. While NH_4ClO_4 and Al had little or no effect on the isocyanate curing agents, plasticizers had a pronounced tendency to consume isocyanates. The hydrocarbon type plasticizers, Nujol, Oronite 6, and Light Circo Oil, consumed only minor amounts of isocyanate; ester type plasticizer, DOZ, IDP and DOS, moderate amounts; and S-141, squalene, and Ansul Ether 181, considerable amounts. The cause was traced to impurities in the commercial plasticizers, and the hydrocarbon and ester types were improved by either contacting them with Linde Molecular Sieves or passing them through a column of silica gel.

(U) E. The gel fraction of cured Telagen S binders indicated that NCO to OH ratio of 1 gave more complete cure than a ratio of 1.05. Cure studies with various catalysts were made, and the results led to the use of FeAA and HAA for curing Telagen S binders and propellants.

(U) F. Binders made with the various prepolymers were extensively characterized, and their behavior correlated with the behavior of the corresponding propellants. Characterization involved cure rate, cure stoichiometry, uniaxial tensile behavior at low, ambient, and high temperatures, solvent swelling, and effect of plasticizers.

(U) G. The effect of plasticizers on the mechanical behavior of the binders was related to the tendency of the plasticizer to interfere with the cure. This cure interference could be mitigated in some instances by pretreatment of the plasticizer. The cure interference by the plasticizer reduced the modulus and gel fraction of the binder which pointed to a decrease of the crosslink density. As a result IDP treated by passage through silica gel became the preferred plasticizer for this program.

(U) H. The solvent swelling of binders in toluene was a very useful technique for the characterization of binders. The Mooney-Rivlin C_1 and the logarithms of σ_m and E_0 were linear functions of the gel fraction. The last two correlations made for binders with 0 to 30% of eight different plasticizers indicated that plasticizers affect mechanical behavior only because they decrease the crosslink densities of binders or conversely that binders with similar crosslink densities whether plasticized or not have similar mechanical behaviors at ambient temperature.

(U) I. The glass transition temperatures of plasticized binders were about -120°F. The use of a plasticizer decreased the binder modulus at -75°F, but the modulus at -75° was a function of the binder modulus at ambient temperature. For this reason, a plasticizer may not be necessary to decrease the low temperature modulus because it can be done by decreasing the crosslink density of the binder to that obtained when a plasticizer is present. The transition observed in the NMR line broadening-temperature relation differed from the T_G by density-temperature measurements. The NMR line broadening transition temperature was more nearly that temperature at which the moduli of Telagen S binders increased rapidly. The NMR transition temperature was roughly linear with the binder gel fraction.

(U) J. Two curing agents, RTDI and C-100, were tried as curing agents. Neither was as effective as the CTI-HDI system currently in use.

(U) K. Solvent swelling of binders with 25 solvents showed that the CED of the Telagen S-CTI-HDI binder was close to 80. For toluene the χ value was 0.497.

(U) L. Telagen S propellants (88 wt% solids) were made and studied in up to 125-lb batches. By processing at 110°F a potlife of almost seven hours was obtained. The propellants were characterized by cure rate, cure stoichiometry, castability, hardness, and uniaxial mechanical behavior at low, ambient, and high temperatures.

(U) M. The cure-interference by plasticizers was present in propellants and adversely affected mechanical behavior. The best NCO to OH ratio for propellant was 1.02.

(C) N. One study of burning rate showed a rate-pressure exponent of 0.7. A high exponent was also obtained for a Telagen S propellant of high (91%) solids loading.

(U) O. A cyclindrically, perforated analogue motor was cycled to failure below -40°F at greater than 14.8% strain.

(C) P. A high solids (91%) propellant was prepared and fully characterized. The technique used was to first determine the best solids particle size blend by a study of Oronite 6 slurries and the use of this blend for preparation of propellant. Extrapolation to large motor performance of ballistic data obtained in 1KS-250 size motor (1-lb propellant) indicated an effective specific impulse of 250 or more than 3 specific impulse units better than predicted for the Minuteman Wing VI second stage propellant. A 60-lb batch showed $\sigma_m = 155$, $\epsilon_m = 11$, and $E_0 = 2100$ at ambient temperature; the failure envelope was derived. The further development of this propellant was strongly recommended.

(U) Q. Prepolymer specifications were written.

(U) R. The compatibility problems associated with the use of Be and LMH-2 were easily overcome and 400-gram scale propellants of these fuels with Telagen S were prepared. When LMH-1 was not compatible with isocyanate, generating CO_2, studies indicated the difficulties were associated with H_2O or OH species adsorbed on the fuel surface. The use of isocyanate cure catalysts and processing and curing at ambient temperature overcame the difficulties, and an LMH-1 propellant (400-gram) was prepared.

(U) S. The main difficulty with the incorporation of HAP or HDP into the Telagen S propellant was the reactivity of these materials with the curing agents. Epoxide and aziridine model compounds were quickly consumed by both HAP and HDP. The isocyanate underwent a small amount of reaction with HAP, but greater amounts of isocyanate were lost in contact with HDP.

(U) T. It was concluded that isocyanate represented the best available curing agent for use with HAP because the side reactions were less serious than those of the other curing agents. With isocyanate-HAP systems, the reaction with alcohols was very fast. In Telagen S propellant systems the short potlife confirmed this fact. A method of slowing the reaction was not found.

(U) U. The rearrangement and polymerization of 1-benzoyl-2-ethylaziridine in contact with various potassium and ammonium salts were studied. Only potassium bromide and iodide caused rearrangement, whereas all the ammonium salts caused some rearrangement. The potassium salts produced mainly 4-ethyl-1-phenyl-2-oxazoline while ammonium salts produced mixtures of 4- and 5-ethyl-1-phenyl-2-oxazoline. Ammonium perchlorate and nitrate caused considerable polymerization of the aziridine.

(U) V. Model oxazolines, thiazolines and imidazolines were not compatible with HAP. After 24 hours at 23°C, all these compounds were consumed by side reactions. The side reactions were not determined.

(U) W. Model systems with both advanced fuel and advanced oxidizers were also studied. The compatibility problems were, of course, increased. In an isocyanate-alcohol-advanced fuel-HAP system, the dominant characteristics were imposed by the HAP. The conclusion was that when the problems associated with the incorporation of HAP were solved, the additional problems associated with the fuel would be less serious.

(U) X. It was discovered that HAP formed crystalline complexes, with one or two moles of hydroxylamine. These complexes, designated HAP-X and HAP-2X, decomposed at their melting point which was roughly the same as HAP and were non-hygroscopic. The densities of these complexes were less than that of HAP. The behavior of these complexes was not further investigated.

(U) Y. Two large scale batches of ammonium perchlorate propellant were placed in aging at from -75 to 170°F under a variety of environments. Because of equipment breakdown, no test results were reported, but the aging is continuing and results will be reported in subsequent reports.

(U) Z. Three propellants made with each of the advanced fuels were prepared and placed in aging. The aging was done at 80°F at 0 and 30% relative humidity. After 4½ months, neither of the propellants made with Be or LMH-2 showed any change of appearance or hardness. No results were reported for the LMH-1 propellant. The aging is continuing.

IV. TECHNICAL PROGRESS (U)

A. MATERIALS (U)

1. Saturated Hydroxy-terminated Hydrocarbon Prepolymers (U)

(U) The work reported in this Final Progress Report was performed with the prepolymer developed under Contract AF 04(611)-10386. The prepolymer was made by The General Tire and Rubber Company according to the tentative requirements in Table I.[1]

Table I

CHARACTERISTICS OF WORKHORSE PREPOLYMER (TELAGEN S) (U)

Backbone	Saturated polybutadiene with about 35% 1,2-addition
Functional Groups	Secondary-OH
Molecular Weight	1500-2000
Functionality	As close to 2 as possible
Viscosity	Less than 100 poises at 50°C

(U) Twenty-two pounds of this prepolymer, Lot 8507-I-47.1, were prepared under Contract AF 04(611)-10386. Some of this material was used to do the work reported here. The properties of this prepolymer are shown in Table II.

(U) Additional saturated prepolymers, both with carboxy and hydroxy functional groups, were acquired and used for this project. The General Tire and Rubber Company is now supplying these prepolymers commercially under the registered trade name Telagen S.

(U) Other hydroxy terminated prepolymers were prepared and delivered under the present contract and were used for some of the work reported here. The properties of these prepolymers are shown in Table II.

2. Saturated, Carboxy-terminated Hydrocarbon Prepolymers (U)

(U) A small amount of saturated hydrocarbon prepolymer with carboxy end-groups was obtained from The General Tire and Rubber Company. The properties of this material are shown in Table III.

3. Unsaturated Prepolymers (U)

(U) In addition to Telagen S, two unsaturated polybutadienes, acid and hydroxy terminated, were received from The General Tire and Rubber Company. The two materials are unsaturated analogs of the Telagen S prepolymers, and were used to make unsaturated binders comparable to those being studied on this program. The properties of the prepolymers are shown in Tables II and III (Lots 242AM-148 A and D). Prepolymer 148AH of Table II is a hydrogenation product of Prepolymer 148A.

4. CTI (U)

(U) Two kilograms of the triisocyanate, CTI, were prepared and purified by recrystallization. The purities of these materials ranged from 93 to 97%.

Table II

PROPERTIES OF HYDROXY-TERMINATED PREPOLYMERS (U)

	Batch Number				
			242AM-		
	242AM-128	8507-I-47.1[a]	148A	148AH[b]	242AM-158H[a]
Molecular Weight					
Theoretical	1766	-	-	-	-
Solution Viscosity	1180	-	-	-	-
VPO	1620	1676[c]	1750	-	1900
Equivalent Weight	953	980	1030	1100	1130
Functionality[d]	1.70	1.71	1.70	1.62[e]	1.68
Unsaturation, mm/g	17.1	0.28	-	0.78	0.69
cis	27.6	-	39.7	-	-
trans	38.3	-	27.3	-	-
vinyl	34.1	-	33.0	-	-
Ash, %	-	0.03	0.004	0.015	< 0.01
Antioxidant 2246, %	0.5	-	-	-	-
Brookfield Viscosity, Poise at 25°C	28	190	29	169	161
Volatiles, %	-	0.1	0.77	0.79	0.36

[a]Twenty-two pound batch.
[b]Forty-five pound batch.
[c]Estimated from VPO molecular weight of the prepolymer and change in unsaturation.
[d]Ratio of VPO molecular weight to equivalent weight.
[e]Assuming a hydrogenated polymer of 1780 molecular weight.

Table III

PROPERTIES OF CARBOXY-TERMINATED PREPOLYMERS (U)

	Batch No. 242AM-	
	148D[a]	148DH3[b]
Molecular Weight	1600	1640
Equivalent Weight	985	1120
Functionality[d]	1.62	1.49[e]
Unsaturation, mm/gm	-	0.05
trans, %	29.2	29.2[c]
cis, %	40.9	40.9[c]
vinyl, %	29.9	29.9[c]
Ash, %	0.0035	0.06
Antioxidant, %	2.09	0.13[f]
Brookfield Viscosity, Poises at 25°C	82	609
Water, %	0.01	0.04
Volatiles, %	0.45	0.18

[a]Unsaturated.
[b]Hydrogenated.
[c]Determination made prior to hydrogenation.
[d]Molecular weight to equivalent weight ratio.
[e]Assuming molecular weight of 1670 for hydrogenated prepolymer.
[f]Estimated value.

(U) At the request of the Rocket Propulsion Laboratory, samples of CTI were sent to Dr. Lloyd McGhee, Thiokol Chemical Corporation, to Mr. Paul Allen, United Technology Corporation, and to Mr. C. Bacon, Air Force Rocket Propulsion Laboratory.

B. PHASE I (U)

1. Introduction (U)

(U) Phase I involved a study of the exact cure stoichiometry of the prepolymer, the effects of various plasticizers on propellant properties, and the maximum achievable solids loading with NH_4ClO_4 and aluminum. The propellant with the highest solids loading was completely characterized with respect to mechanical behavior and was evaluated ballistically at the 1-lb level. The specifications for the prepolymer were established.

2. Prepolymer Characterization (U)

a. Molecular Weight and Functionality Distributions (U)

(U) A sample of Telagen S (Lot 8507-I-47.1; Table II) was fractionated on a 40A-permeability-limit polystyrene gel column. Average number molecular weight by Vapor Phase Osmometry and equivalent weight by Nuclear Magnetic Resonance Spectrometry were established for each fraction. The results are shown in Table IV. The two results marked with an asterisk were considered doubtful, since the fraction weights were too little for accurate analysis by the procedure used.

Table IV

MOLECULAR WEIGHT AND FUNCTIONALITY DISTRIBUTIONS[a] OF TELAGEN S[b] (U)

Fraction	Fraction Wt.	% of Total	Eq. Wt.[c]	Mol. Wt.[d]	Functionality
1	0.0915	6.0	915*	2050	2.2
2	0.4321	28.3	1143	1678	1.5
3	0.4802	31.5	1021	1607	1.6
4	0.3136	20.6	888	1507	1.7
5	0.1769	11.6	884	1430	1.6
6	0.0313	2.0	321*	920	2.9
Average[e]	-	-	-	1606	1.65

[a]Gel permeation chromatographic separation recovery 99.33%.
[b]See Table II; Lot 8507-I-47.1.
[c]By NMR analysis of end groups.
[d]By VPO
[e]Averaging fractions; compare with molecular weight of 1622 and functionality of 1.66 determined on the unfractionated sample.

(U) If one neglects the doubtful values, the functionality did not vary with the molecular weight of the prepolymer. Typically an unsaturated polybutadiene showed an increase in functionality with molecular weight (Figure 1)[2]. This difference between polybutadienes and Telagen S was ascribed to either the saturated nature of the latter which cannot be oxidatively polymerized to give a higher molecular weight, higher functionality material or to the narrower molecular weight range of Telagen S which did not allow the increase of functionality with molecular weight to be detected.

(U) This determination of the functionality of the prepolymer agreed well with the determination made under Contract AF 04(611)-10386 and shown in Table II.

(U) A sample of Lot 242AM-148AH was sent to the Esso Research and Engineering Company for evaluation and their results have been made public[3]. They reported a very wide molecular weight distribution (400 to 7000) by both gel permeation chromatography and by osmodialysis, but the two methods did not agree on the amounts of low-molecular weight fractions. Our gel permeation data were consistent with those of the Esso workers, but at this time our experience with Telagen S makes us skeptical of the osmodialysis results as regards the amount of the low-molecular weight fraction. If the same results could be obtained with a different type of membrane, the osmodialysis results would be more strongly supported.

b. Functionality (U)

(U) The functionality of a prepolymer has always been of utmost importance and is perhaps the most important single factor which determines the nature of the polymer network in binders and propellants. (Functionality determinations by various methods have given widely varying results.)

(U) The expected functionality of Prepolymer 8507-I-47.1 from molecular weight (vapor phase osmometry) divided by equivalent weight (end-group titration) was 1.7. Theoretically a binder of this prepolymer reacted with a 4 to 1 equivalents mixture of HDI and CTI should not cure but actually well cured binders were obtained (Table XI, Binders 5 and 27). Using the crosslink densities determined from compression moduli of the swollen Binders 5 and 20 (Table XI), and the equation for crosslink density

$$X_D = \sum_{i=1}^{i=n} \frac{(f_i - 2)W_i}{f_i E_i} \quad \text{(moles of crosslinks/gm of binder)}$$

where
- i = the binder ingredient
- n = the number of binder ingredients
- f = the functionality of the ingredient
- W = the weight fraction of the ingredient
- E = the equivalent weight of the ingredient

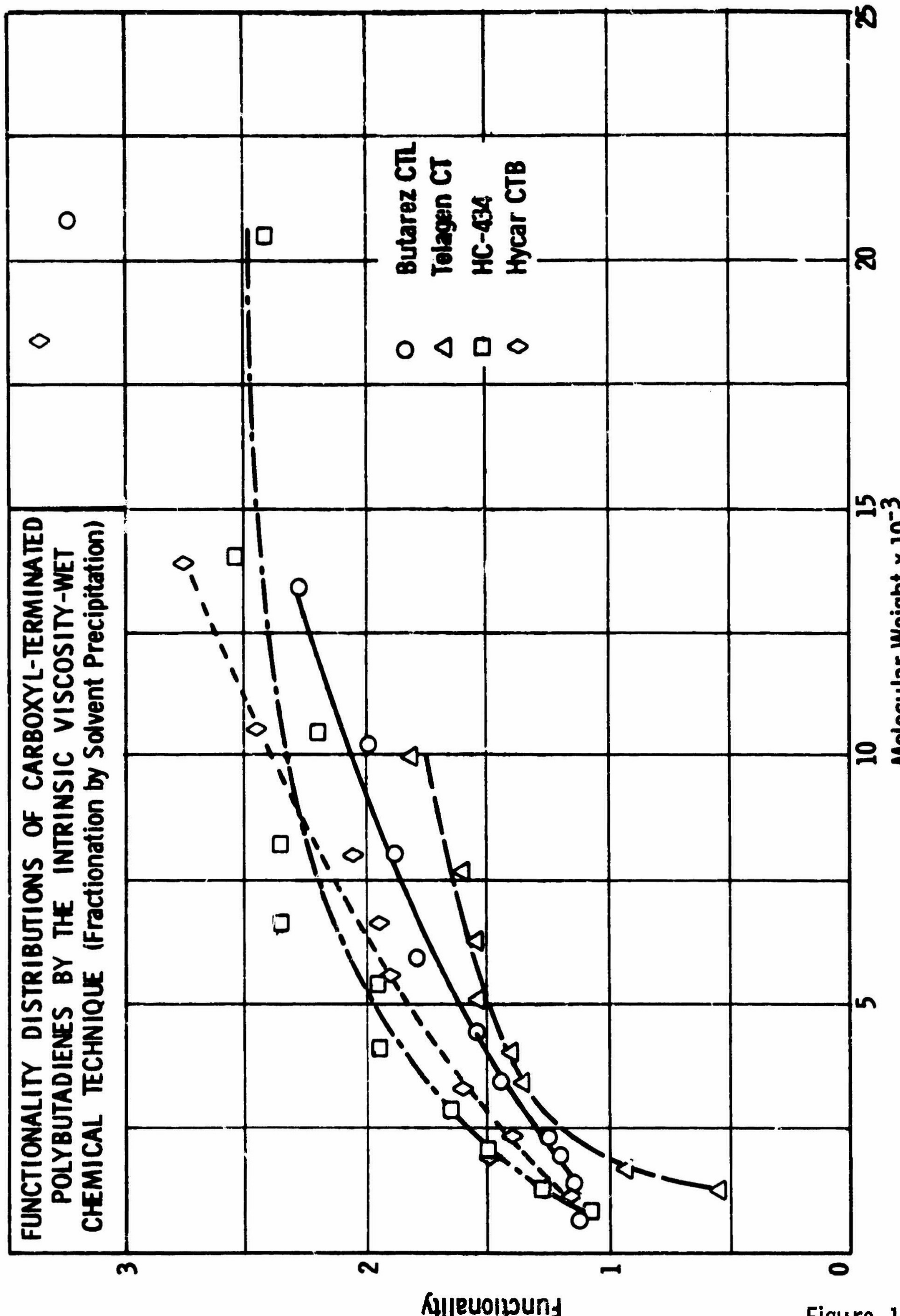
FUNCTIONALITY DISTRIBUTIONS OF CARBOXYL-TERMINATED POLYBUTADIENES BY THE INTRINSIC VISCOSITY-WET CHEMICAL TECHNIQUE (Fractionation by Solvent Precipitation)
Butarez CTL
Telagen CT
HC-434
Hycar CTB
Functionality
0
1
2
3
5
10
15
20
25
Molecular Weight x 10^-3

Figure 1

one derived an effective functionality of 1.90. This agreed well with the effective functionality of 1.88 determined for the same prepolymer from the equilibrium moduli during the previous program[1].

(U) Two binders with a calculated crosslink density of zero were prepared from Prepolymer 8507-I-47.1. One was based on the expected functionality of 1.7 (Binder 44, Table XI) and the other on the effective functionality of 1.88 (Binder 45, Table XI). Both of the binders were swollen in toluene; the gel fractions of Binders 44 and 45 were 0.1808 and 0.0718, respectively. This favors the effective functionality value in the range 1.85 to 1.90 because the gel fraction of Binder 45 was nearer to zero.

(U) In these experiments, the amounts of extractables from the two binders were similar. This may indicate the presence of nonfunctional material or low molecular weight prepolymer which was not tied into either of the networks.

(U) The HDI to CTI ratio used to cure these binders also indicates a prepolymer functionality of approximately 1.90. A prepolymer with a functionality of 1.5, requires a trifunctional curing agent to achieve initial crosslinking, while a prepolymer with a functionality of 2.00 requires only a trace of trifunctional curing agent to achieve crosslinking. At a functionality of 1.7, 70 parts of the trifunctional curing agent and 30 parts of the difunctional curing agent are needed, and at a functionality of 1.90, 20 parts of the tri- and 80 parts of the difunctional agent are required for crosslinking. In these experiments, a 4 to 1 ratio of HDI to CTI was used to achieve a soft (low crosslink density) binder. At an HDI to CTI ratio of 30 to 70, one obtains a very hard (high crosslink density) binder.

(U) On the basis that the extractable materials were mainly non-functional and the prepolymer tied into the network contained all of the -OH groups, a calculation predicted a functionality of about 2.1 for the functional units. This was an encouraging result when the approximations involved were considered.

(U) For the formulation of binders and propellants, the effective functionality was more useful than the expected functionality. The differences between the two can be explained by the presence of nonfunctional material in the prepolymer. While association of chains, hydrogen bonding, entanglements, etc., will effect the value of functionality determined from the mechanical behavior of a binder, these effects were minimized by making measurements on a swollen binder.

(U) Several binders were prepared from Prepolymer 242AM-148AH at various ratios of HDI to CTI and at equal equivalents of isocyanate and prepolymer. The Mooney-Rivlin C_1 constant increased with the increase of the ratio of CTI to total isocyanate (Figure 2). Extrapolation indicated that $C_1 = 0$ (zero crosslink density) at an HDI to CTI ratio of about 6.15. Calculations by this method indicate a functionality of 1.9 for the prepolymer.

C_1 CONSTANT vs. CTI TO ISOCYANATE RATIO FOR TELAGEN S (242 AM - 148 AH)

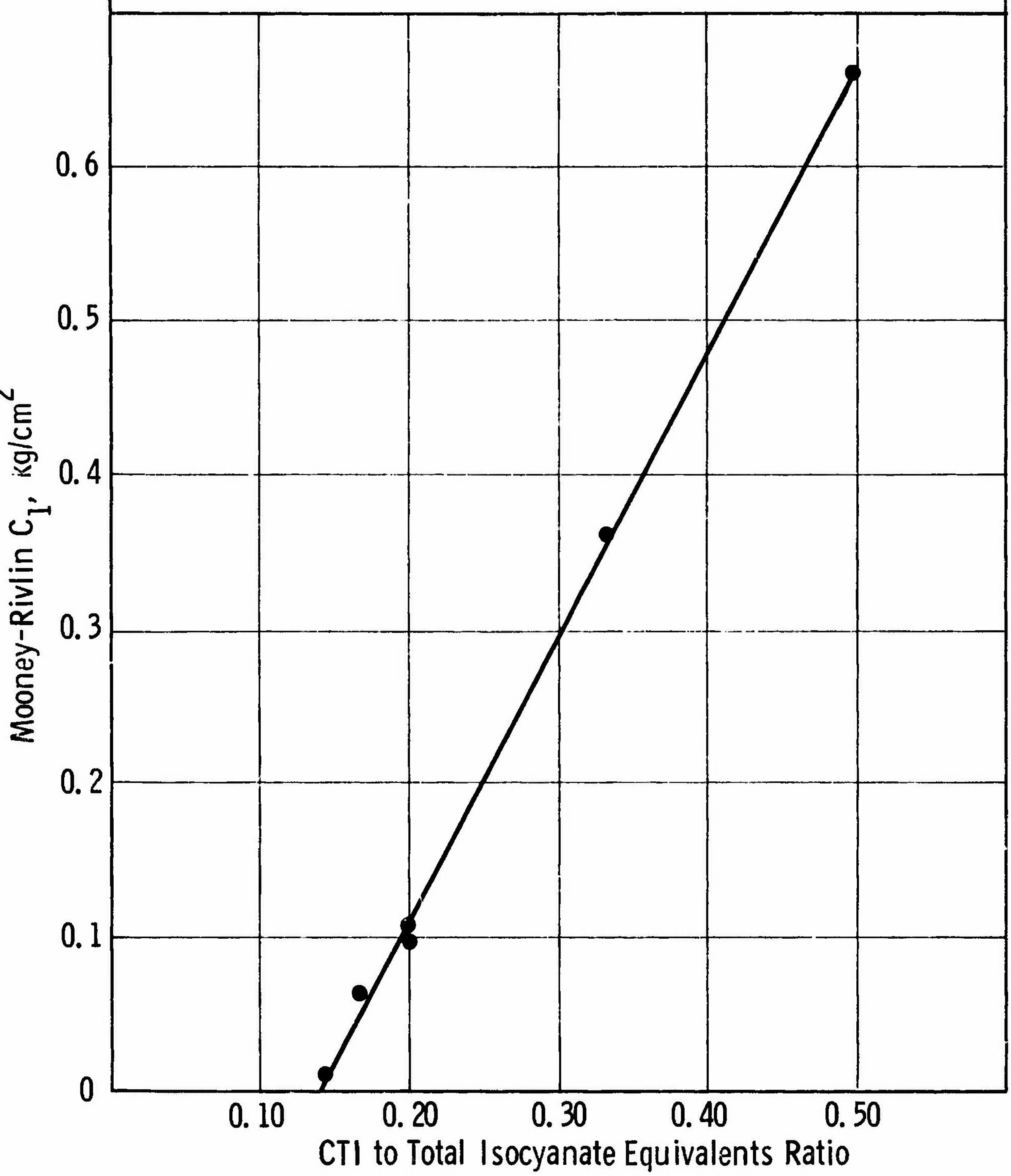

Figure 2

(U) The binder studies indicated that Prepolymer 158H did not have as high a functionality as 148AH. This was readily discernible from a comparison of Binders 77, 100, and 102 with Binders 87, 101, 103, of Binder 98 with Binders 85 and 99, and of Binder 96 with Binder 97; all in Table XI. The conclusion is consistent with the results obtained by workers at The General Tire and Rubber Company, who found Williams Plasticity values of 186 and 252, respectively, for gum-stocks made with the two prepolymers.

(U) While these comparisons could be made and a valid conclusion drawn, obtaining a numerical measure of the difference in functionality was not as sure a procedure. Using the crosslink densities of Binders 100 and 101, one obtained minimum functionalities of 1.91 for prepolymer 148AH and 1.88 for Prepolymer 158H. The small differences between these two numbers and the real difference observed in binder properties raised some doubt as to whether numerical values of functionality could be effective as specifications for this type of prepolymer. At this time a specification based on properties such as hardness, gel fraction, and Williams Plasticity for a polymer made in a standard fashion has been designated as a measure of functionality.

c. Other Comparisons of the Prepolymers (U)

(U) Three lots of prepolymer were used for the experiments reported here. Their properties are summarized in Table II. Lot 242AM-148AH, the largest (45 lb) batch of Telagen S delivered to Aerojet to date, was more reddish and cured faster than the older Lot 8507-I-47.1. One binder made with Lot 242AM-148AH, containing Light Circo Oil, cured within 7 days without additional catalyst; however, it had a soft surface. The propellants made with these prepolymers were similar, indicating similar functionalities.

(U) Prepolymer 242AM-158H was a translucent white material and not reddish as Prepolymer 242AM-148AH. Its rate of cure was about the same as that of 8507-I-47.1.

3. Effect of NH_4ClO_4 on Isocyanate Curing Agents (U)

(U) Phenyl isocyanate in toluene was used to determine the effect of NH_4ClO_4 on the isocyanate curing agents. Some of the NH_4ClO_4 samples were fresh and others had been stored on the shelf for 1 year. The particle sizes were 405 μ and 10 μ. None of the samples showed an isocyanate loss greater than the control after 6 days at room temperature. The conclusion is that NH_4ClO_4 would have a negligible effect on the isocyanate curing agents during the time necessary to cure a propellant.

4. Effect of Aluminum Metal on Isocyanate Curing Agents (U)

(U) The loss of isocyanate functionality was measured for toluene solutions of HDI (0.5 gm in 5 gm) both in the absence and presence of aluminum powder (1 gm in 5 gm of solution). With aluminum (30-40 μ spherical particles) present, solutions both with and without FeAA catalyst did not show greater loss of isocyanate than when the metal was absent. This demonstrated that aluminum had little or no effect upon the cure stoichiometry of Telagen S propellants.

5. Plasticizer Studies (U)

a. Effect of Plasticizers on Curing Agents (U)

(U) A very pronounced effect of plasticizers on the curing agents was noted, and the influence of this effect on the properties of both binders and propellant was readily apparent. The effect of the plasticizers on the curing agents seemed to originate with the impurities in the plasticizers. The impurities reacted with the curing agents and lowered the cross-link density of the plasticized binder. This made the determination of the plasticizing action of a plasticizer very difficult.

(U) The effect of the plasticizers on the curing agents was determined by following the disappearance of the isocyanate in a solution containing a plasticizer (5 gm), HDI or phenyl isocyanate (0.5 gm) and a drop of catalyst (Niax D-22 or 0.5 gm FeAA in 10 ml. toluene). A summary of the results is shown on Tables V and VI. The quantity 100-(%NCO remaining in test solution/fraction NCO remaining in control solution) was designated the cure-interference index. This index for each plasticizer was correlated with the mechanical behavior of binders and propellants containing the plasticizer.

(U) The cure-interference indices in Tables V and VI are not the same for a given plasticizer because the indices were derived from data obtained at different conditions. The indices in Table VI were taken from 18 hour data and those in Table V, from 5-day data. In 18 hours the observed changes in the isocyanate content were less so the spread of the indices are less than the corresponding variables after 5 days. The important factor is the relative order of the plasticizers and the relation of the indices to mechanical behavior of binders and propellants. The cure-interference indices can be derived in any laboratory for any functional group (epoxide or aziridine) at any set of conditions. The indices would be consistent and useful within any given method of deriving them.

b. Cure-Interference by Treated Plasticizers (U)

(U) It was apparent that the plasticizers contained impurities or adulterants which seriously disrupted the cure stoichiometry of a binder or a propellant. Since many of these plasticizers were designed especially for use in solid propellants and conformed to specifications consistent with this use, a further study of the problem was made.

(U) Of the plasticizers studied, the saturated hydrocarbons (oils) caused the lowest cure-interference index. The commonly used plasticizers, DOZ and IDP, caused a large loss of isocyanate functionality.

(U) IDP and squalene were each dried over "Dri Na", a sodium-lead alloy, and over 4A Molecular Sieve pellets. The plasticizer was decanted from the solids and the disappearance of isocyanate in each of the dried plasticizers was determined. The results shown in Table VII indicated a definite improvement for IDP as evidenced by the lower cure-interference indices (compare Table V) while for squalene very little, if any, improvement was indicated.

Table V

EFFECT OF PLASTICIZERS ON HDI[a] (U)

Plasticizer	Plasticizer Dried[b]	Isocyanate Remaining, %[c]	Cure-Interference Index[d]
Toluene (Control)	yes	92.6	0.0
Nujol	yes	92.3	0.1
Oronite-6	yes	88.6	4.2
Light Circo Oil	yes	87.0	5.9
n-Undecyl Cyanide	no	84.4	8.7
IDP	no	76.2	17.7
DOZ	yes	74.8	19.2
Citroflex	no	70.7	23.6
Squalene	no	70.2	24.2
S-141	yes	68.4	26.0
Methyl N-butylcarbamate	no	58.8	36.4
Tetraethylene Glycol Dimethyl Ether	no	51.0	44.9

[a] Test solution consisted of plasticizer (5 gm), HDI (0.5 gm), Niax D-22 (1 drop).
[b] Plasticizers dried over Molecular Sieve 4A except toluene, which was distilled from sodium.
[c] After 5 days at room temperature.
[d] 100-(% isocyanate remaining/.926).

Table VI

EFFECT OF PLASTICIZERS ON HDI[a] (U)

Plasticizer	Plasticizer Dried[b]	Isocyanate Remaining, %[c]	Cure-Interference Index[d]
Toluene (Control)	yes	101	0.0
Nujol	yes	99.4	1.5
Light Circo Oil	yes	98.6	2.2
DOZ	yes	96.0	4.8
IDP	no	94.0	6.8
Squalene	no	84.6	16.1
Tetraethylene Glycol Dimethyl Ether	no	74.2	26.5

[a]Test solution consisted of plasticizer (5 gm), HDI (0.5 gm), and FeAA.
[b]Plasticizers dried over Molecular Sieve 4A except toluene, which was distilled from sodium.
[c]After 18 hours at room temperature.
[d]100-(% NCO remaining/1.01).

Table VII

EFFECT OF DRIED PLASTICIZERS ON PHENYL ISOCYANATE[a] (U)

Plasticizer	Drying Agent	Isocyanate Remaining, %[b]	Cure-Interference Index[c]
IDP	Dri Na	86	7.0
	Molecular Sieve	92	0.5
Squalene	Dri Na	54	41.7
	Molecular Sieve	73	21.0

[a]Test solution consisted of plasticizer (5 gm), phenyl isocyanate (0.5 gm) and FeAA.
[b]After 3 days at room temperature.
[c]100-(% NCO remaining/.926).

(U) The plasticizers dried over "Dri Na" had a haze in them, possibly a fine precipitate of products from the reaction of impurities with the sodium. These products could act as basic catalysts for the isocyanate-consuming reactions, so that this method of drying would not be a useful treatment of plasticizers, unless the haze-causing materials were subsequently removed.

(U) In further studies on IDP and squalene, both materials were passed through a column of silica gel and their effect on isocyanate loss determined (Table VIII). This treatment definitely reduced the amount of cure interference by both IDP and squalene.

Table VIII

EFFECT OF PLASTICIZER TREATMENT ON PHENYL ISOCYANATE[a] (U)

Plasticizer	Treatment[b]	Isocyanate Remaining, %[c]	Cure-Interference Index[d]
Toluene	none	100	0.0
	yes	99	0.1
IDP	none	94	6.0
	yes	98	2.0
Squalene	none	85	15.0
	yes	98	2.0

[a] Test solution consisted of plasticizer (5 gm), phenyl isocyanate (0.5 gm) and FeAA.
[b] Passed through a column of silica gel.
[c] Untreated samples tested after 18 hours and treated ones after 16 hours at room temperature.
[d] 100-(% NCO remaining).

(U) Tetraethylene glycol dimethyl ether (Ansul Ether 181) could not be purified on silica gel. In fact, the ether which was passed through silica gel caused greater cure-interference than the original (Table IX). Ansul Ether 181 (150 ml.) was passed through a column of silica gel (100-200 mesh, 1 in. diam x 8 in.) and fractionated into eight cuts (each about 7.5 gm). The remainder was taken as one large fraction. The effect of the first and fifth fractions on phenyl isocyanate was compared with the effect of the unfractionated material (Table IX).

(U) The unfractionated plasticizer caused less loss of phenyl isocyanate than the fractionated materials, but even the original plasticizer prevented the cure of binders.

Table IX

EFFECT OF ANSUL ETHER 181 ON PHENYL ISOCYANATE[a] (U)

Ansul Ether 181	Isocyanate Remaining, %[b]	Cure-Interference Index[c]
Untreated	53	42.7
Fractionated (Fraction 5)[d]	13.5	85.4
Fractionated (Fraction 1)[d]	0.7	100.0

[a]Test solution consisted of Ansul Ether (5 gm), phenyl isocyanate (0.5 gm), and FeAA.
[b]After 3 days at room temperature.
[c]100-(% NCO remaining/.926)
[d]Ansul Ether fractionated into eight fractions and a residue by passage through a column of silica gel.

(U) S-141 was partially purified by passing it through a column of silica gel, but this treatment did not remove all of the impurities. Silica gel removed the yellow color from Oronite-6 and n-undecyl cyanide, but neither compound, the purified or "as received", showed any significant reduction of isocyanate assays over a period of 8 days. Work with binders confirmed that these plasticizers did not interfere with the isocyanate.

c. Infrared Analysis of Plasticizer Impurities (U)

(U) Large yellow bands which formed in the silica gel columns were eluted and studied by near infrared. The IR spectrum of "as received" IDP showed two impurity peaks - probably water and hydroxyl containing material. The spectrum of the impurities eluted from the column showed a decrease of the water peak, but the other peak was increased (Figure 3). Both spectra were taken with the purified IDP in the reference cell. With squalene, a carbonyl peak, which could be an ester or an aldehyde, was found in the "as received" sample (Figure 4). No further attempts were made to identify these peaks.

d. Cure-Interference Index for Purified Squalene (U)

(U) Squalene was purified and the loss of isocyanate dissolved in it determined. One portion of the squalene was purified by passage through a column of silica gel and another portion was redistilled under vacuum. These results shown in Table X indicated that impurities in the squalene were affecting the isocyanates. These impurities were not further identified.

COMPARISON OF INFRARED SPECTRA OF "AS RECEIVED" IDP AND IDP PURITIES (PURIFIED IDP IN REFERENCE CELL)

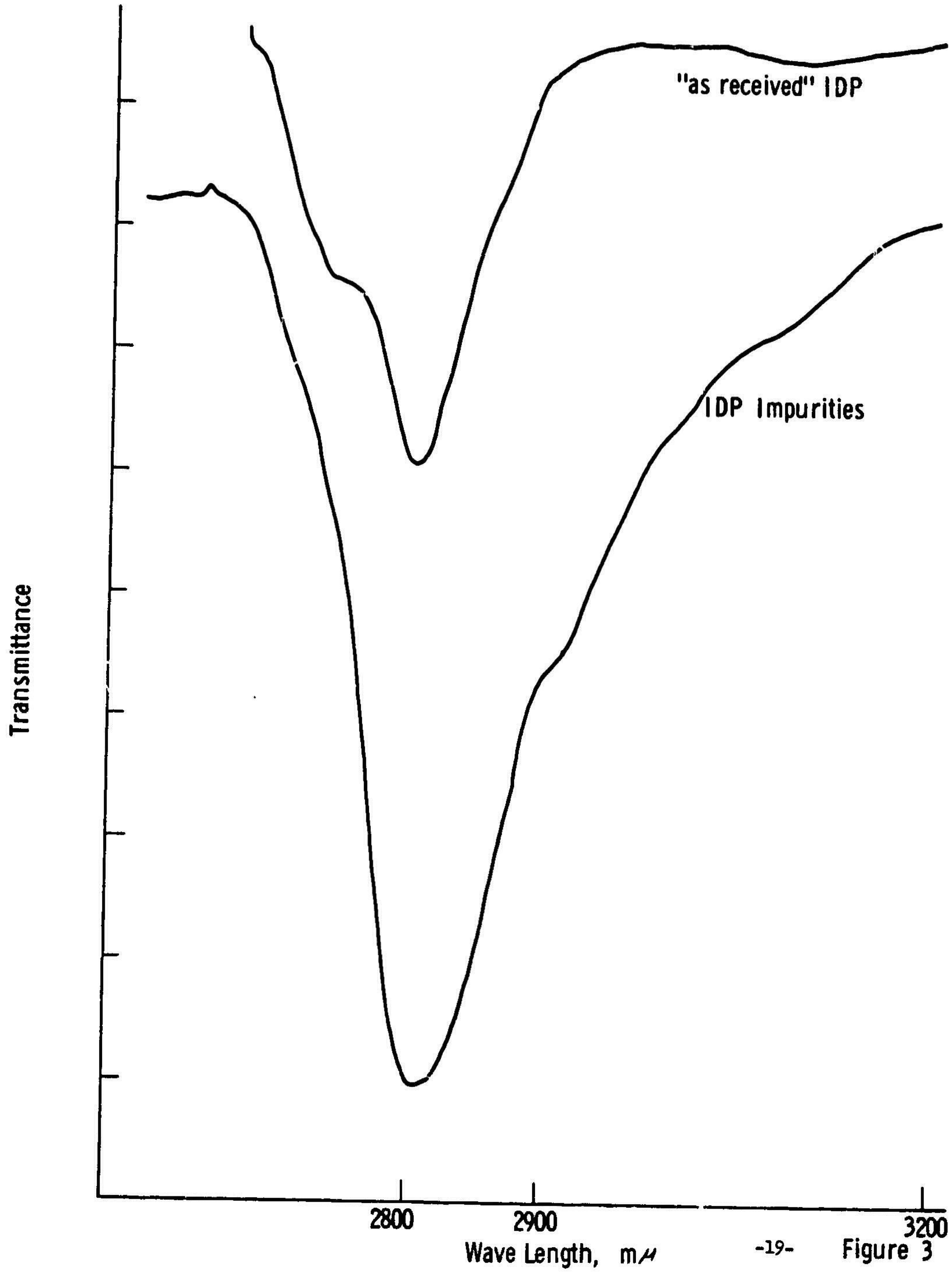

 Figure 3

COMPARISON OF INFRARED SPECTRA OF "AS RECEIVED" SQUALENE AND PURIFIED SAMPLE

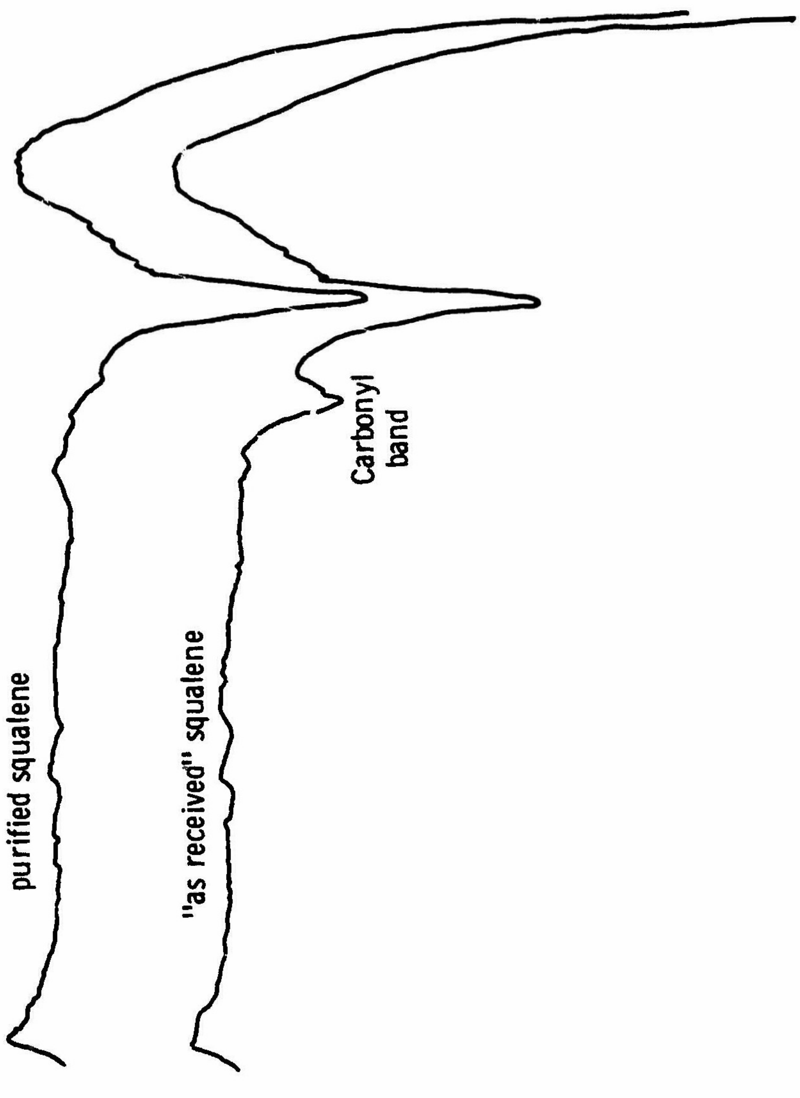

Figure 4

(U) Purifying the plasticizers generally gives better binder properties. The use of vacuum redistilled squalene improved the binder properties (Table XI, Nos. 11 and 32) but squalene-plasticized binders still had poorer properties than other hydrocarbon plasticized binders.

Table X

EFFECT OF PURIFIED SQUALENE ON HDI AND PHENYL ISOCYANATES[a] (U)

Purification	Isocyanate[b]	Isocyanate Remaining, %[c]	Cure-Interference Index[d]
None	HDI	37	60
	PhNCO	50	46
Through Silica Gel	HDI	76	18
	PhNCO	60	35
Redistilled,	HDI	84	9
	PhNCO	82	11

[a]Test solution consisted of 5 gm of plasticizer, 0.5 gm of isocyanate and FeAA.
[b]Hexamethylene diisocyanate and phenyl isocyanate.
[c]Four days at ambient temperature.
[d]100-(% NCO remaining/.926).

e. Cure-Interference of Redistilled IDP (U)

(U) A sample of redistilled IDP (Emery Industries) caused a rapid loss in the isocyanate when tested with HDI. This plasticizer was used in Binder 31 (Table XI) and the poor cure confirmed that it did interfere with the cure reaction. Obviously the distillation served to concentrate rather than to remove the offending contaminants. These results also demonstrated the effectiveness of the test to predict at least qualitatively the mechanical behavior of binders containing the plasticizer.

f. Cure-Interference of Arneel OD (U)

(U) Arneel OD, oleyl nitrile, was investigated as a plasticizer for Telagen S binders. The binder (Table XI, No. 46) did not cure in 24 days at 135°F. Arneel OD had been used in other programs with propellants containing MAPO and BISA (aziridine) curing agents. These propellants had poorer mechanical properties and aging stability than propellants containing the plasticizer IDP. Passing Arneel OD through a column of silica gel improved the propellant properties which, however, were still inferior to those of IDP plasticized binders. These results demonstrated that problems of plasticizer interference with curing reactions might be common to all curing systems and have gone unnoticed because softening of the binders by the cure interference has been confused with plasticizing action.

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Table XI

COMPOSITION AND PROPERTIES OF TELAGEN S

Reference No.	Prepolymer Lot No.[a]	Plasticizer	% Wt.	Plasticizer Treatment[b]	HDI/CTI	NCO/OH	Cure Time,[c] Days at 135°F	Mechanical Properties σ_m psi	ϵ_m %
1	8507-I-47.1	none	0.0	none	4.0	1.05	7	65	358
2	8507-I-47.1	IDP	10.0	SiO_2	4.0	1.05	7	37	325
3	8507-I-47.1	IDP	20.0	SiO_2	4.0	1.05	7	31	375
4	8507-I-47.1	IDP	30.0	SiO_2	4.0	1.05	7	20	365
5	8507-I-47.1	none	0.0	none	4.0	1.00	6	74	478
6	8507-I-47.1	IDP	20.0	SiO_2	4.0	1.00	6	43	536
7	8507-I-47.1	Squalene	25.0	SiO_2	4.0	1.05	6	23	520
8	8507-I-47.1	IDP	20.0	none	4.0	1.00	6	30	510
9	8507-I-47.1	S-141	25.0	MS	4.0	1.00	6	15	510
10	8507-I-47.1	S-141	25.0	SiO_2	4.0	1.00	6	20	510
11	8507-I-47.1	Squalene	25.0	none	4.0	1.00	6	13	690
12	8507-I-47.1	Squalene	25.0	MS	4.0	1.00	6	-	-
13	8507-I-47.1	Squalene	25.0	SiO_2	4.0	1.00	6	-	-
14	8507-I-47.1	Ansul Ether 181	25.0	none	4.0	1.00	6	dissolved	
15	8507-I-47.1	$C_{11}H_{23}CN$	25.0	none	4.0	1.00	3	28	425
16	8507-I-47.1	$C_{11}H_{23}CN$	25.0	SiO_2	4.0	1.00	3	30	500
17a	8507-I-47.1	IDP	25.0	SiO_2	4.0	1.00	0.75	24	480
17b	8507-I-47.1	IDP	25.0	SiO_2	4.0	1.00	2	22	440
17c	8507-I-47.1	IDP	25.0	SiO_2	4.0	1.00	5	26	450
17d	8507-I-47.1	IDP	25.0	SiO_2	4.0	1.00	14	30	476
17-1	8507-I-47.1	Oronite 6	25.0	MS	4.0	1.05	10	48	400
17-2	8507-I-47.1	DOZ	25.0	MS	4.0	1.05	10	46	472
17-3	8507-I-47.1	S-141	25.0	MS	4.0	1.05	10	39	506
17-4	8507-I-47.1	Light Circo Oil	25.0	none	4.0	1.05	10	52	404
18	8507-I-47.1	DOZ	26.3	none	4.0	1.00	5	23	511
18A	8507-I-47.1	DOZ	26.3	none	4.0	1.00	3	23	540
19	8507-I-47.1	DOZ	26.3	SiO_2	4.0	1.00	5	28	454
20	8507-I-47.1	Light Circo Oil	22.9	MS	4.0	1.00	5	48	566
21	8507-I-47.1	$C_{11}H_{23}CN$	24.2	SiO_2	4.0	1.00	6	25	482
22	8507-I-47.1	Oronite 6	24.5	SiO_2	4.0	1.00	6	25	764
23	8507-I-47.1	S-141	29.5	none	4.0	1.00	6	17	779
24	8507-I-47.1	Light Circo Oil	9.1	MS	4.0	1.00	5	65	406
25	8507-I-47.1	Light Circo Oil	18.2	MS	4.0	1.00	5	44	372
26	8507-I-47.1	Light Circo Oil	27.7	MS	4.0	1.00	5	34	430
27	8507-I-47.1	none	0.0	none	4.0	1.00	6	96	425
28	8507-I-47.1	IDP	10.0	SiO_2	4.0	1.00	6	63	380
29	8507-I-47.1	IDP	20.0	SiO_2	4.0	1.00	6	41	355
30	8507-I-47.1	IDP	30.0	SiO_2	4.0	1.00	6	36	435
31	8507-I-47.1	IDP	25.0	Red.	4.0	1.00	6	Did not cu	
32	8507-I-47.1	Squalene	24.9	Red.	4.0	1.00	6	40	775
37	8507-I-47.1	DOS	26.2	none	4.0	1.00	6	-	-
38	8507-I-47.1	Squalene	24.9	Red.	4.0	1.00	6	-	-
39	242AM-148A	IDP	25.0	SiO_2	3.0	1.00	6	-	-
40	242AM-148A	IDP	25.0	SiO_2	4.0	1.00	6	-	-
41	8507-I-47.1	Squalane	25.0	Red.	4.0	1.00	6	-	-
42	8507-I-47.1	Oronite 6	24.6	MS	4.0	1.00	6	-	-
43	8507-I-47.1	Nujol	25.2	MS	4.0	1.00	6	-	-
44	8507-I-47.1	none	0.0	none	0.54	1.00	6	-	-

Table XI

PROPERTIES OF TELAGEN S BINDERS (U)

Cure Time,[c] Days at 135°F	Mechanical Properties σ_m psi	ϵ_m %	ϵ_b %	E_0 psi	Mooney-Rivlin C_1 kg/cm²	C_2 kg/cm²	Crosslink Density[d] moles of chain/cc x 10^5 A	B	C	Gel Fraction v_2	Sol Fraction[e]
7	65	358	358	72	0.28	0.57	1.7	-	2.6	0.091	0.23
7	37	325	325	41	0.22	0.26	1.6	3.2	2.5	0.081	0.26
7	31	375	375	23	0.15	0.17	1.2	2.0	1.8	0.067	0.23
7	20	365	365	16	0.10	0.10	1.2	1.3	1.4	0.057	0.25
6	74	478	478	69	0.23	0.57	1.9	3.4	2.3	0.079	0.24
6	43	536	537	22	0.14	0.16	1.2	-	1.7	0.063	0.25
6	23	520	-[f]	15	0.07	0.12	0.61	0.90	0.90	0.044	0.37
6	30	510	-[f]	20	0.10	0.13	1.0	-	-	0.054	0.28
6	15	510	-[f]	13	0.05	0.11	0.70	-	-	0.041	-
6	20	510	-[f]	16	0.07	0.11	0.82	-	-	0.050	-
6	13	690	-[f]	8	-	-	-	-	-	0.029	-
6	-	-	-	-	-	-	-	-	-	0.030	-
6	-	-	-	-	-	-	-	-	-	0.028	-
6	dissolved in toluene and trichloroethylene										
3	28	425	425	21	0.12	0.13	0.95	-	-	0.059	-
3	30	500	500	18	0.10	0.12	0.98	-	-	0.056	-
0.75	24	480	-[f]	14	0.095	0.093	0.80	-	-	0.056	0.35
2	22	440	440	16	0.10	0.096	1.1	-	-	0.058	0.25
5	26	450	450	19	0.1	0.11	0.99	-	-	0.060	0.24
14	30	476	476	19	0.12	0.11	1.1	-	-	0.060	-
10	48	400	400	34	0.20	0.24	1.9	2.6	2.4	0.076	0.19
10	46	472	472	24	0.16	0.17	1.6	2.2	2.0	0.069	0.24
10	39	506	506	26	0.13	0.16	1.3	1.8	1.7	0.061	-
10	52	404	404	32	0.20	0.25	2.3	3.0	2.7	0.073	0.27
5	23	511	511	13	0.084	0.070	0.78	-	-	0.050	0.28
3	23	540	540	12	0.079	0.074	0.58	-	-	0.050	0.37
5	28	454	454	20	0.11	0.11	1.2	-	-	0.060	0.22
5	48	566	566	31	0.13	0.19	1.4	-	-	0.067	0.22
6	25	482	482	19	0.095	0.095	0.89	-	-	0.052	-
6	25	764	764	17	0.028	0.016	0.36	-	-	0.038	-
6	17	779	803	6	0.033	0.046	0.28	-	-	0.027	-
5	65	406	406	60	0.25	0.48	-	-	-	0.089	-
5	44	372	372	48	0.20	0.32	-	-	-	0.078	-
5	34	430	430	29	0.14	0.18	-	-	-	0.062	-
6	96	425	425	84	0.34	0.70	-	-	-	0.097	-
6	63	380	380	56	0.26	0.41	-	-	-	0.087	-
6	41	355	355	36	0.22	0.20	-	-	-	0.070	-
6	36	435	435	23	0.16	0.11	-	-	-	0.065	-
6	Did not cure completely.										
6	40	775	775	18	-	-	-	-	-	0.044	-
6	-	-	-	-	-	-	-	-	-	0.058	-
6	-	-	-	-	-	-	-	-	-	0.028	-
6	-	-	-	-	-	-	-	-	-	0.066	-
6	-	-	-	-	-	-	-	-	-	0.046	-
6	-	-	-	-	-	-	-	-	-	0.067	-
6	-	-	-	-	-	-	-	-	-	0.073	-
6	-	-	-	-	-	-	-	-	-	0.073	-
6	-	-	-	-	-	-	-	-	-	0.181	-

Table XI Continued

Reference No.	Prepolymer Lot No.[a]	Plasticizer	% Wt.	Plasticizer Treatment[b]	HDI / CTI	NCO / OH	Cure Time,[c] Days at 135°F	σ, psi
45	8507-I-47.1	none	0.0	none	4.25	1.00	6	-
46	8507-I-47.1	Arneel-OD	25.0	SiO_2	4.0	1.00	24	Did
46-1	8507-I-47.1	Squalene	25.0	MS	4.0	1.05	10	18
46-2	8507-I-47.1	Nujol	25.0	MS	4.0	1.05	10	43
46-3	8507-I-47.1	IDP	25.0	none	4.0	1.05	-	34
47	242AM-148AH	IDP	25.0	SiO_2	4.0	1.00	7	-
48A	8507-I-47.1	Light Circo Oil	22.9	MS	4.0	1.00	7[g]	-
48B	8507-I-47.1	Light Circo Oil	22.9	MS	4.0	1.00	5	-
49	242AM-148AH	none	0.0	none	1.75	1.00	6	-
50	242AM-148AH	none	0.0	none	1.03	1.00	6	-
51	242AM-148AH	none	0.0	none	0.48	1.00	6	-
52	242AM-148AH	IDP	25.0	SiO_2	4.0	1.00	6[h]	-
53	242AM-148AH	IDP	25.0	SiO_2	4.0	1.00	6[i]	-
54	242AM-148AH	IDP	25.0	SiO_2	4.0	1.00	6	-
55	242AM-148AH	IDP	25.0	SiO_2	4.0	1.00	6[j]	-
56	242AM-148AH	IDP	25.0	SiO_2	4.0	1.00	6[k]	-
57[l]	242AM-148AH	DOS	26.1	SiO_2	4.0	1.05	12	-
58[l]	242AM-148AH	Light Circo Oil	23.0	MS	4.0	1.05	12	-
59[l]	242AM-148AH	$C_{11}H_{23}CN$	24.2	none	4.0	1.05	12	-
60	242AM-148AH	none	0.0	none	4.0[m]	1.05	12	-
61	242AM-148AH	IDP	25.0	SiO_2	4.0[m]	1.05	12	-
62	242AM-148AH	none	0.0	none	4.0[n]	1.05	6	-
63	242AM-148AH	IDP	25.0	none	4.0[n]	1.05	6	-
64	242AM-148D	Arneel-OD	25.0	none	-[o]	1.00[o]	10[o]	-
65	242AM-148D	IDP	25.0	SiO_2	-[o]	1.00[o]	10[o]	-
66	242AM-148D	none	0.0	none	-[o]	1.00[o]	10[o]	-
67	242AM-148DH-3	Arneel-OD	25.0	none	-[o]	1.00[o]	10[o]	-
68	242AM-148DH-3	IDP	25.0	SiO_2	-[o]	1.00[o]	10[o]	-
69	242AM-148DH-3	none	0.0	none	-[o]	1.00[o]	10[o]	-
75	242AM-148AH	none	0.0	none	6.0	1.00	7	10
76	242AM-148AH	none	0.0	none	5.0	1.00	7	27
77	242AM-148AH	none	0.0	none	4.0	1.00	7	29
78	242AM-148AH	none	0.0	none	2.0	1.00	7	59
79	242AM-148AH	none	0.0	none	1.0	1.00	7	82
85	242AM-158H	IDP	25.0	SiO_2	4.0	1.00	6	36
86	242AM-158H	none	0.0	none	2.5	1.00	6	-
87	242AM-158H	none	0.0	none	4.0	1.00	6	54
96	242AM-148AH	none	0.0	none	4.0[m]	1.00	6	38
97	242AM-158H	none	0.0	none	4.0[m]	1.00	6	18
98	242AM-148AH	IDP	25.0	SiO_2	4.0	1.00	4	16
99	242AM-158H	IDP	25.0	SiO_2	4.0	1.00	4	20
100	242AM-148AH	none	0.0	none	4.0	1.00	5	-
101	242AM-158H	none	0.0	none	4.0	1.00	5	-
102	242AM-148AH	none	0.0	none	4.0	1.00	5	84
103	242AM-158H	none	0.0	none	4.0	1.00	5	78

*Please see notes on following page.

Table XI Continued

CO H	Cure Time,[c] Days at 135°F	Mechanical Properties σ_m psi	ϵ_m %	ϵ_b %	E_0 psi	Mooney-Rivlin C_1 kg/cm²	C_2 kg/cm²	Crosslink Density[d] moles of chain/cc x 10⁵ A	B	C	Gel Fraction v_2	Sol Fraction[e]
.00	6	-	-	-	-	-	-	-	-	-	0.072	-
.00	24	Did not cure.[f]										
.05	10	18	458	-[f]	11	0.08	0.07	0.49	0.81	0.68	0.042	-
.05	10	43	354	355	34	0.20	0.21	1.0	3.11	2.45	0.081	-
.05	-	34	450	462	22	0.14	0.13	1.2	1.6	1.6	0.063	-
.00	7	-	-	-	-	-	-	-	-	-	0.048	-
.00	7[g]	-	-	-	-	-	-	-	-	-	0.039	-
.00	5	-	-	-	-	-	-	-	-	-	0.060	-
.00	6	-	-	-	-	-	-	-	-	-	0.110	-
.00	6	-	-	-	-	-	-	-	-	-	0.179	-
.00	6	-	-	-	-	-	-	-	-	-	0.226	-
.00	6[h]	-	-	-	-	-	-	-	-	-	0.070	-
.00	6[i]	-	-	-	-	-	-	-	-	-	0.061	-
.00	6	-	-	-	-	-	-	-	-	-	0.072	-
.00	6[j]	-	-	-	-	-	-	-	-	-	0.071	-
.00	6[k]	-	-	-	-	-	-	-	-	-	0.059	-
.05	12	-	-	-	-	-	-	-	-	-	0.067	-
.05	12	-	-	-	-	-	-	-	-	-	0.075	-
.05	12	-	-	-	-	-	-	-	-	-	0.070	-
.05	12	-	-	-	-	-	-	-	-	-	0.040	-
.05	12	-	-	-	-	-	-	-	-	-	0.020	-
.05	6	-	-	-	-	-	-	-	-	-	0.066	-
.05	6	-	-	-	-	-	-	-	-	-	0.057	-
.00[o]	10[o]	-	-	-	-	-	-	-	-	-	0.136	-
.00[o]	10[o]	-	-	-	-	-	-	-	-	-	0.133	-
.00[o]	10[o]	-	-	-	-	-	-	-	-	-	0.189	-
.00[o]	10[o]	-	-	-	-	-	-	-	-	-	0.112	-
.00[o]	10[o]	-	-	-	-	-	-	-	-	-	0.128	-
.00[o]	10[o]	-	-	-	-	-	-	-	-	-	0.152	-
.00	7	10	575	575	6	0.010	0.08	0.15	-	-	0.029	-
.00	7	27	460	460	26	0.063	0.23	0.57	-	-	0.050	-
.00	7	29	400	400	34	0.10	0.22	0.84	-	-	0.061	-
.00	7	59	280	280	56	0.36	0.30	3.02	-	-	0.106	-
.00	7	82	200	200	126	0.66	0.58	6.40	-	-	0.150	-
.00	6	36	580	580	14	-	-	-	-	-	0.043	-
.00	6	-	-	-	-	-	-	-	-	-	0.101	-
.00	6	54	620	620	38	-	-	-	-	-	0.054	-
.00	6	38	530	530	59	-	-	-	-	0.81	0.060	-
.00	6	18	-[f]	-[f]	40	-	-	-	-	0.15	0.030	-
.00	4	16	300	300	15	-	-	-	-	1.30	0.054	-
.00	4	20	518	518	14	-	-	-	-	0.63	0.034	-
.00	5	-	-	-	-	-	-	-	-	1.68	0.075	-
.00	5	-	-	-	-	-	-	-	-	0.68	0.043	-
.00	5	84	280	280	97	-	-	-	-	-	0.098	-
.00	5	78	630	630	53	-	-	-	-	-	0.055	-

Table XI Footnote:

[a]Prepolymer properties given in Tables II and III.

[b]MS = contacted with Linde Molecular Sieves; SiO_2 = passed through column of silica gel; I

[c]Samples contained FeAA as cure catalyst unless otherwise specified.

[d]A = from compression moduli of swollen samples; B and C = from equilibrium moduli by stre

[e](weight of extractables - weight of plasticizer)/(weight of sample - weight of plasticize

[f]Bond failure or no break.

[g]No cure catalyst added.

[h]Niax D-22 used as cure catalyst.

[i]Niax D-22 plus HAA used as cure catalysts.

[j]FeAA plus HAA used as cure catalysts.

[k]CoAA used as cure catalyst.

[l]Binder contains 0.8% C-1.

[m]HDI replaced by RTDI.

[n]HDI replaced by TDI.

[o]Acid-terminated prepolymer cured with C-100 at acid to aziridine ratio of 1 and no cure c

Table XI Footnotes

through column of silica gel; Red. = redistilled.

specified.

from equilibrium moduli by stress relaxation at 77 and 150°F, respectively.

of sample - weight of plasticizer).

iridine ratio of 1 and no cure catalyst.

6. Binder Studies (U)

a. Introduction (U)

(U) Binders were prepared and studied by mechanical behavior, solvent-swelling, glass transition, and by nuclear magnetic resonance spectroscopy. The data were correlated with the effects of prepolymer functionality, the effects of plasticizer, and the effects of curing stoichiometry. The binder studies are summarized in Table XI.

b. Cure Stoichiometry (U)

(U) Studies with unplasticized binders indicated that the optimum cure stoichiometry was at an NCO to OH ratio of from 1.0 to 1.05 Table XII).

Table XII

EFFECT OF NCO TO OH RATIO ON THE GEL FRACTION OF TELAGEN S BINDERS[a] (U)

Reference No.	Prepolymer No.	NCO/OH	Gel Fraction
102	242AM-148AH	1.00	0.098
27	8507-I-47.1	1.00	0.079
1	8507-I-47.1	1.05	0.091
5	8507-I-47.1	1.00	0.079
100	242AM-148AH	1.00	0.075
77	242AM-148AH	1.00	0.061
60	242AM-148AH	1.05[b]	0.040
96	242AM-148AH	1.00[b]	0.060

[a]Details of composition in Table XI; HDI/CTI = 4.0.
[b]HDI replaced by RTDI.

(U) The highest gel fractions were obtained with an NCO to OH ratio of 1.0. Since a larger sampling of binders with an NCO to OH ratio of 1.05 was not available, the conclusions were not absolutely certain. It was permissible to compare binders made with Prepolymer 8507-I-47.1 with those made with 242AM-148AH because these prepolymers were of the same functionality.

(U) Figure 5 shows the effect of stoichiometry on the gel fractions of IDP-plasticized binders. The figure shows clearly that the gel fractions of binders made at an NCO to OH ratio of 1.00 are higher than those of binders made at a ratio of 1.05.

c. Catalysts (U)

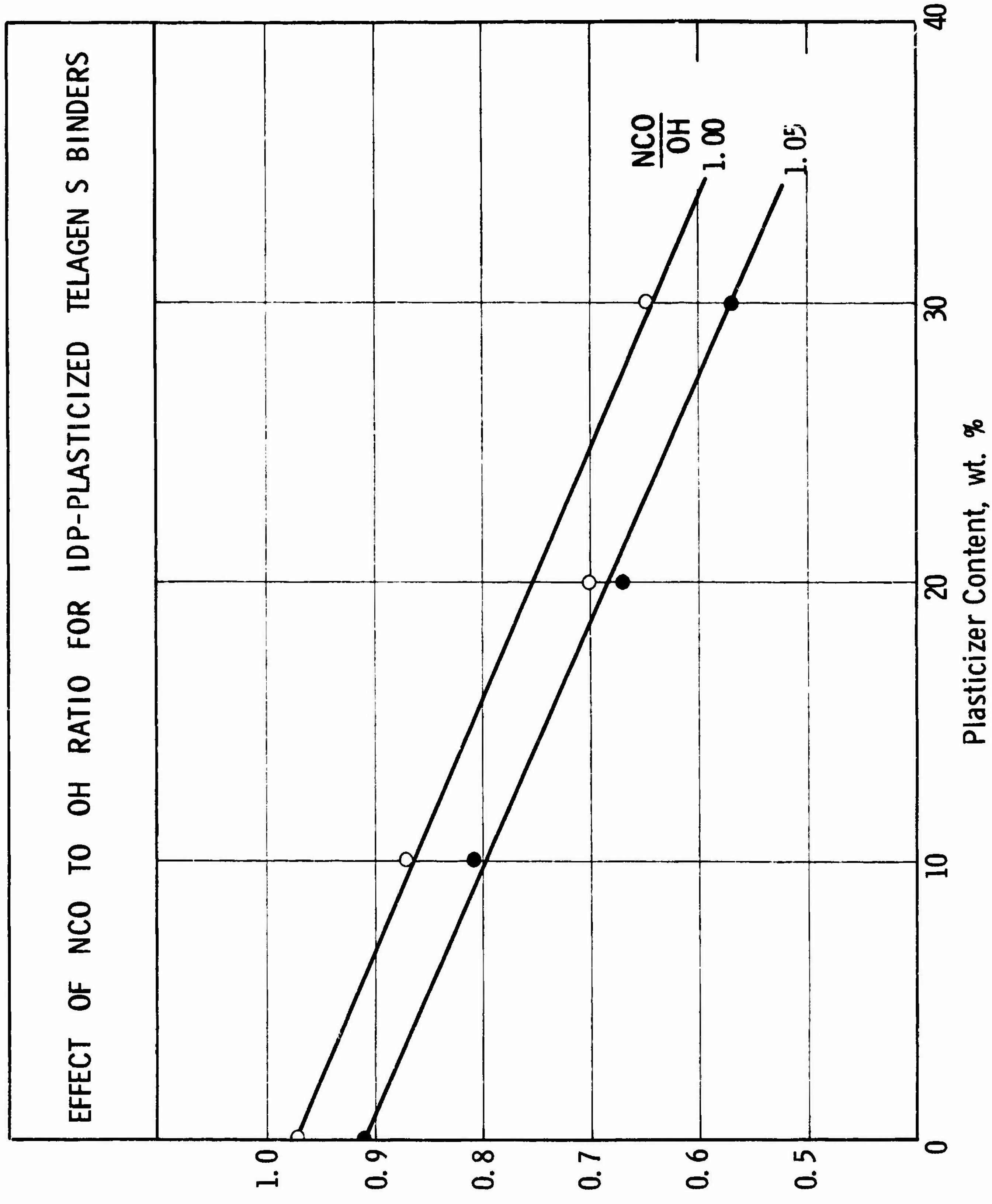
(U) Hydroxy-terminated Telagen S, Lot 148AH, was used to determine the efficiencies of several catalysts. The catalysts, which were used on an equimolar basis, included CoAA, FeAA, Niax D-22, and FeAA and Niax D-22 with added acetylacetone (Table XIII). The cure of binders with CoAA was slower and less efficient in this system than with the other catalysts, as determined by the gel fraction of the binders. Niax D-22 was as active as FeAA in catalyzing the cure of this binder. The binder gel fractions indicated that while HAA interfered with the extent of cure when used with Niax D-22, it did not when used with FeAA. As a result of these studies the combination of FeAA + HAA was used as a cure catalyst for preparation of propellants.

Table XIII

THE EFFECT OF VARIOUS CATALYSTS ON THE EXTENT OF CURE OF TELAGEN S BINDERS[a] (U)

Reference No.	Catalyst	Co-Catalyst	Gel Fraction
52	Niax D-22	none	0.070
53	Niax D-22	HAA	0.061
54	FeAA	none	0.072
55	FeAA	HAA	0.071
56	CoAA	none	0.059

[a]Binder composition and properties given in Table XI. The catalyst were all equimolar with respect to the metal.



EFFECT OF NCO TO OH RATIO FOR IDP-PLASTICIZED TELAGEN S BINDERS

Figure 5

(U) The use of HAA was shown by Oberth and Bruenner[4] to decrease the catalytic effect of FeAA on the isocyanate-alcohol reaction. According to these workers the decreased catalysis was the result of shifting the following equilibrium to the left by added HAA.

$$Fe(AA)_3 + HOR \rightleftarrows Fe(AA)_2\,OR + HAA$$

The catalytic specie might be $Fe(AA)_2\,OR$. The HAA would affect only the rate of cure and not the extent.

(U) The Telagen S, Lot 148AH, was redder in color than the previous material, Lot 8507-I-47.1, and cured faster. Light Circo Oil and IDP plasticized binders were prepared for comparison with those made with the older batch of prepolymer. Gel fractions indicated that binders prepared with Lot 148AH had a lower crosslink density than those prepared with the earlier lot. However, the propellant properties were nearly comparable. One binder prepared from Lot 148AH, containing Light Circo Oil, cured reasonably well within seven days, without additional catalyst. The cause of the more rapid cure rate of Lot 148AH is not known.

d. Effect of Plasticizers (U)

1) Introduction (U)

(U) Binders were prepared for the study of plasticizers and their effect on mechanical properties and glass transition temperatures. The binders were made at NCO to OH ratios of 1.00 and 1.05. The combination of mechanical properties and solvent swelling data allowed differentiation of binder-plasticizer interactions from the plasticizer-curing agent interactions which reduce the number of crosslinks. The mechanical properties of the plasticized binder were dependent upon both the plasticizing effect (binder-plasticizer interaction) and the effect on the cure reaction (curing agent-plasticizer interaction). On the other hand, the swelling behavior was dependent only on cure reaction, i.e., the number of crosslinks formed. The results of these studies could be correlated with the cure-interference of the plasticizer (see Section IV.B.5).

2) Mechanical Properties (U)

(U) Mechanical property data have been summarized in Table XI. These data allowed tentative conclusions concerning the effects of plasticizers on the properties of binders.

(U) The results indicated that binders plasticized with IDP or DOZ had better properties when the plasticizer was passed through a column of silica gel. The use of squalene or S-141 passed through silica gel also improved binder properties. The hydrocarbon plasticizers, Oronite, Light Circo Oil, and Nujol, gave the best properties.

(U) The data demonstrated that those plasticizers which showed the greatest effect on the curing agents had a great effect on the mechanical properties. The effect was to degrade the mechanical behavior

(lower break tensile and lower modulus), and the mechanical properties were improved in some cases by treatment of the plasticizer.

(U) The data in Table XIV showed that the mechanical behavior of the plasticized binder was generally related to the cure-interference index of the plasticizer. Many more examples could be found by a careful study of Table XI. While some correlations could be found which were not in the exact order shown in Table XIV, the general relationship between the cure-interference index of a plasticizer and the mechanical behavior of the plasticized binder was very firmly established.

Table XIV

CURE-INTERFERENCE INDICES OF PLASTICIZERS AND THE MECHANICAL BEHAVIOR OF PLASTICIZED TELAGEN S BINDERS[a] (U)

Reference No.	Plasticizer	Cure-Interference Index[b]	Mechanical Behavior at 77°F σ_{m} psi	ϵ_{m} %	E_0 psi	Gel Fraction
5	none	0.0	74	478	69	.079
43	Nujol	0.3	-	-	-	.073
42	Oronite-6	4	-	-	-	.073
20	Light Circo Oil	6	48	566	31	.074
15	n-Undecyl Cyanide	9	28	425	21	.059
17C	IDP	18	26	450	19	.060
19	DOZ	19	28	454	20	.062
11	Squalene	24	13	690	8	.029
22	S-141	26	17	779	6	.027

[a]Plasticizer content 26 vol %; binder composition, Table XI.
[b]Table V.

(U) Some plasticizers were pretreated by various methods which included passage through a column of silica gel, drying over Linde Molecular Sieves (4A), and redistillation. In many cases pretreatment notably improved the mechanical behavior of a plasticized binder (Table XV). Some exceptions were noted. Binders plasticized with n-undecyl cyanide which had been passed through a column of silica gel were not improved over the binder containing untreated plasticizer.

Table XV

EFFECT OF PRETREATMENT OF PLASTICIZER ON THE MECHANICAL BEHAVIOR OF PLASTICIZED TELAGEN S BINDERS[a] (U)

Reference No.	Plasticizer	Plasticizer Treatment[b]	Mechanical Behavior at 77°F σ_m psi	ϵ_m %	E_0 psi	Gel Fraction
15	$C_{11}H_{23}CN$	none	28	425	21	0.059
16	$C_{11}H_{23}CN$	SiO_2	30	500	18	0.056
21	$C_{11}H_{23}CN$	SiO_2	25	482	19	0.052
8	IDP	none	30	510	20	0.054
6	IDP	SiO_2	43	536	22	0.063
18	DOZ	none	23	511	13	0.050
19	DOZ	SiO_2	28	454	20	0.060
11	Squalene	none	13	690	8	0.029
32	Squalene	Red.	40	775	18	0.044

[a]Binder composition in Table XI.
[b]SiO_2 = passed through column of Silica Gel;
MS = contacted with Linde Molecular Sieves;
Red. = redistilled.

(U) As the result of these studies and corresponding work with propellants, IDP treated by passage through a column of silica gel was used for large-scale propellant work.

(U) There was a straight line relationship between the Mooney-Rivlin C_1 and volume fraction of binder for a series of binders with increasing amounts of IDP (Figure 6). The logarithm of the tensile or of the initial modulus versus volume fraction of plasticizer gave a linear relationship when plotted on semilog paper (Figure 7). These correlations were not consistent with theory. Treloar gives the relation $G' = Gv_2^{⅓}$ for the dependence of the modulus of a swollen rubber, G', on the modulus of the unswollen rubber, G, and the gel fraction.[5] If the plasticized binder can be treated as a swollen rubber, the modulus and the Mooney-Rivlin C_1 should vary as the one third power of the volume fraction of binder. The direct dependence of the mechanical behavior parameters on the volume fraction of binder was noted repeatedly and well substantiated.

3) Stress Relaxation (U)

(U) The uniaxial stress relaxation properties of some plasticized binders at 77° and 150°F are shown in Table XVI. The equilibrium moduli for the binder was converted to equilibrium moduli for the networks (unplasticized system) by dividing the former by the volume fraction of network. The equilibrium moduli were higher for those plasticizers which affect the curing agents least. This is indicated in Figure 8. The relaxation times are also shown, but these did not indicate any well defined trend.

Table XVI

STRESS RELAXATION PROPERTIES OF SOME PLASTICIZED BINDERS[a] (U)

Reference No.	Plasticizer	Content vol %	Temp °F	Initial Modulus psi	Equilibrium Modulus, psi Binder	Network[c]	Apparent τ^b min	Recovery %
17-3	S-141	21.7	77	25	16.1	20.3	284	94
			150	21	17.1	21.6	1520	94
17-2	DOZ	24.8	77	31	20.1	26.7	418	83
			150	21	19.9	26.5	1780	99
17-1	Oronite-6	26.5	77	30	23.2	31.6	340	97
			150	26	24.8	33.8	1075	97
17-4	Light Circo Oil	28.3	77	39	26.2	36.5	394	85
			150	30	27.0	37.6	743	97

[a]Binder composition in Table XI.
[b]Relaxation time = time for tensile to be reduced to 1/e of initial value.
[c]Network modulus = binder modulus/vol. fraction network; stress relaxation determined at 25% elongation.

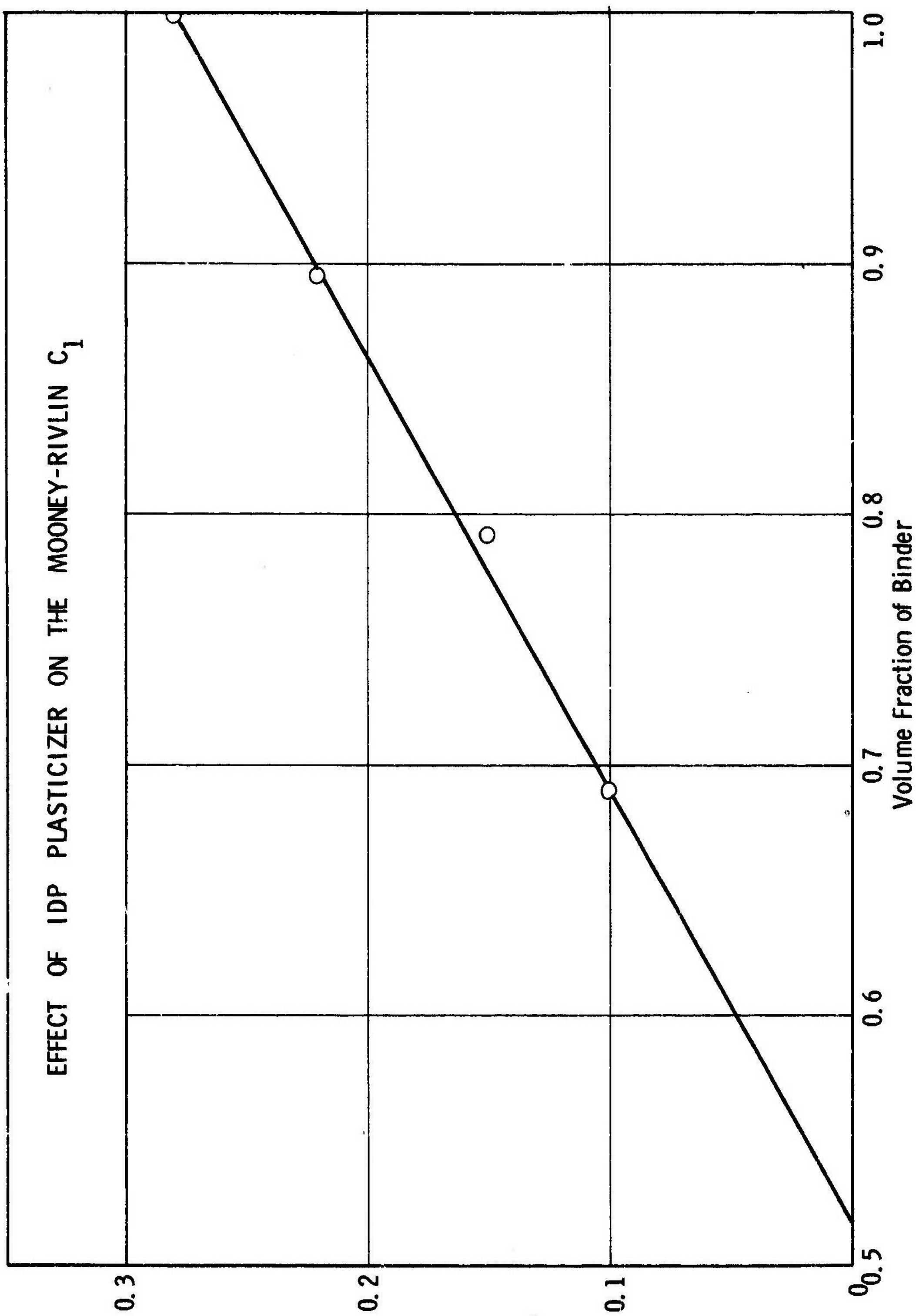

EFFECT OF IDP PLASTICIZER ON THE MOONEY-RIVLIN C_1
0.3
0.2
0.1
0
0.5
0.6
0.7
0.8
0.9
1.0
Volume Fraction of Binder
Mooney-Rivlin C_1, kg/cm^2

Figure 6

EFFECT OF IDP CONTENT ON THE MAXIMUM TENSILE STRESS AND MODULUS OF TELAGEN S-CTI-HDI BINDERS

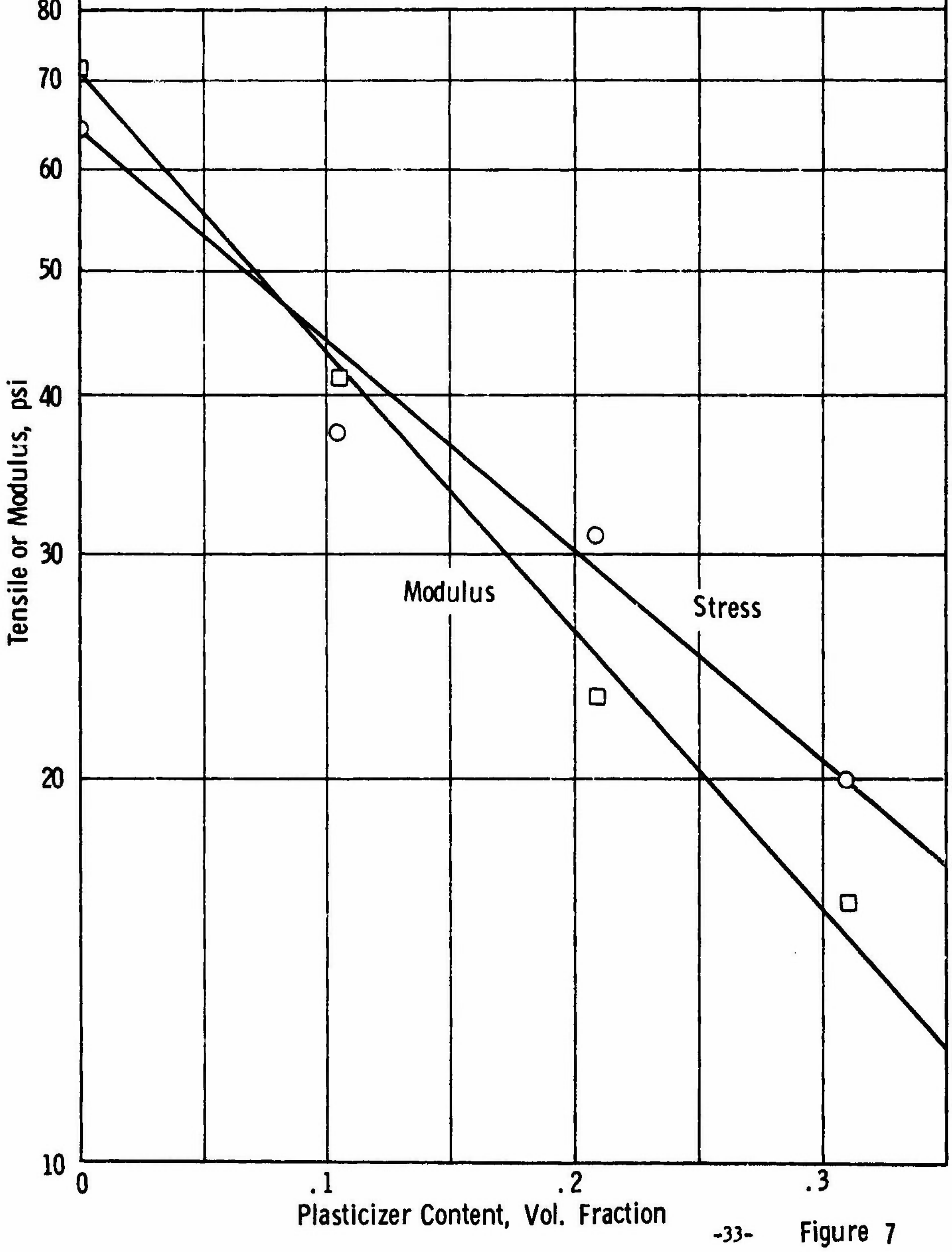


Figure 7

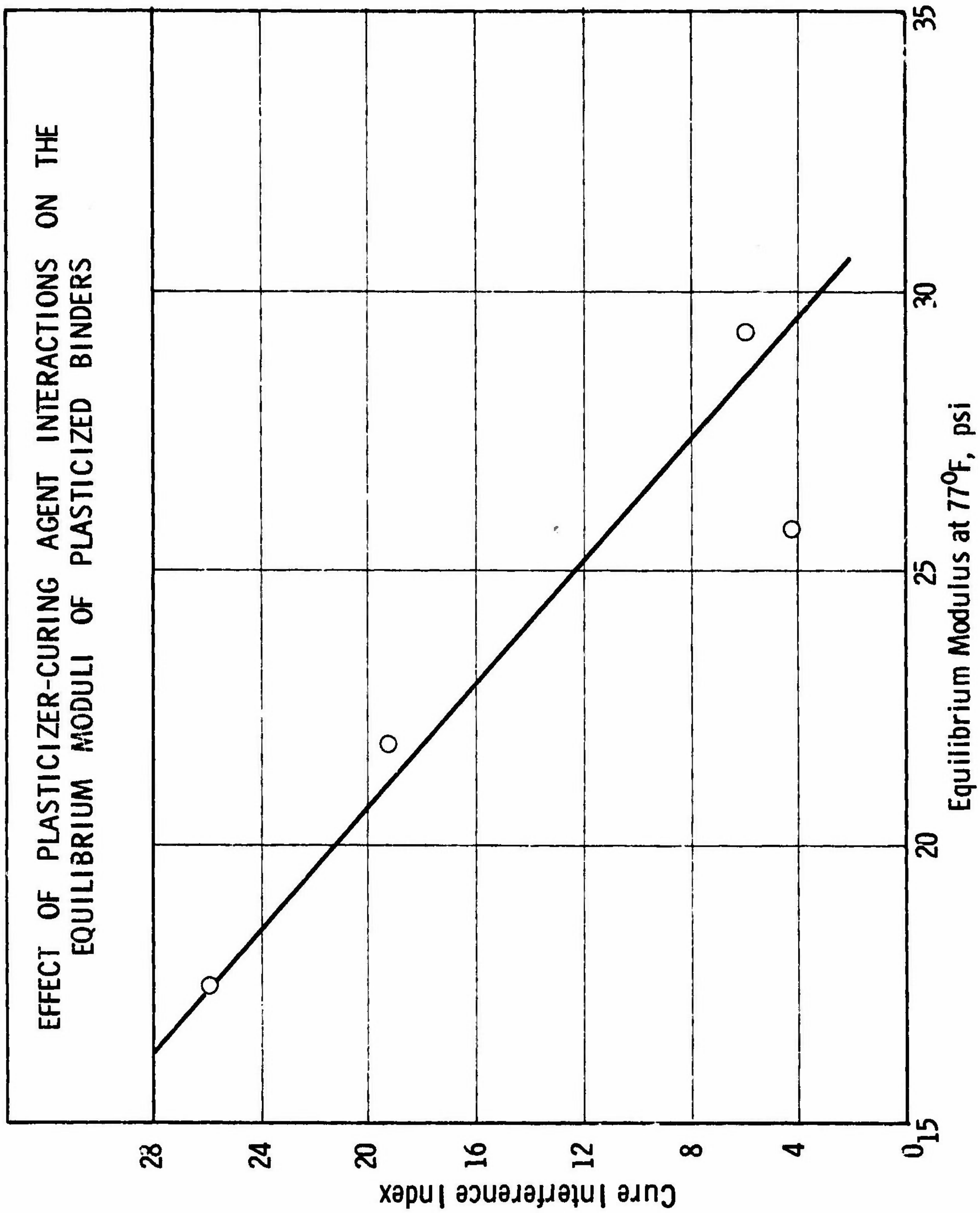


Figure 8

UNCLASSIFIED

4) Swelling of Plasticized Binders (U)

(U) The solvent swelling of binders was a very useful tool for studying the effect of plasticizers. Unlike the mechanical behavior of binders which was affected both by the cure-interference and plasticizing effect of a plasticizer, the gel fraction measured only the cure-interference. The gel fractions of plasticized binders, even those plasticized with materials of very little cure-interference, were always less than those of unplasticized binders. This indicated that binders cured in the presence of plasticizers, even when the plasticizer interferes very little with the cure reaction, always had a lower gel fraction (lower crosslink density) than had binders cured without plasticizer. The cause of this difference was not pursued.

(U) A study was made to determine the best swelling solvent and from the results (see Section IV.B.6.g.) toluene was selected and used exclusively for solvent swelling studies.

(U) Table XVII shows the effect of swelling some of the binders listed in Table XI. The solvent was toluene. Again the effect of the plasticizers on the curing agents was very apparent. Table XVIII and Figure 9 demonstrate the effect of plasticizer-curing agent interaction on gel fraction. As indicated in Table XVIII, there was also a qualitative relation between the effect of the plasticizer on the rate of the isocyanate reaction and the gel fraction.

(U) That the change in mechanical properties on plastication of a binder was not simply the effect of plasticizer-binder interaction, was shown by other correlations with the gel fraction of swollen binders. Figure 10 shows the Mooney-Rivlin C_1 constant for the plasticized binders vs the gel fraction of the binder. Figures 11 and 12 relate the gel fractions to the logarithms of the maximum uniaxial tensile strengths and the initial uniaxial moduli of the binders. Both showed considerable scatter. These curves were of great importance because they indicated that for the systems studied, the maximum tensile strength and the initial tensile modulus depended only on the gel fraction (or crosslink density). This dependence was not affected by the presence of a plasticizer, by type of plasticizer(8), by amount of plasticizer (0 to 30 wt%), by some minor changes in curing agents (HDI replaced by TDI or RTDI), and by NCO to OH ratio.

(U) The plasticizer still affected the mechanical behavior of the binder, but it was doing so only because it affected the gel fraction (crosslink density) of the binder. The data implied that a non-plasticized binder with the same gel fraction (crosslink density) would behave mechanically the same as the plasticized binder notwithstanding the nature or content of the plasticizer. This idea is a radical departure from what has been the prevalent idea concerning plasticization of propellant binders.

(U) These data do not constitute proof because they were obtained for only one binder system, an isocyanate-cured Telagen S. The data are scattered as data of these types usually are, but the importance of the idea warrants further investigation.

Table XVII

GEL AND SOL FRACTION FOR PLASTICIZED BINDERS[a] SWOLLEN IN TOLUENE (U)

Reference No.	Plasticizer	Content Wt%	Treatment[b]	Time to Maximum Swelling, days	Gel Fraction	Sol Fraction
5	none	0.0	none	8	0.079	0.24
8	IDP	20.0	none	8	.054	.28
6	IDP	20.0	SiO_2	8	.063	.25
17a	IDP	25.0	SiO_2	-	.056	.35
17b	IDP	25.0	SiO_2	6	.058	.25
17c	IDP	25.0	SiO_2	6	.060	.24
17d	IDP	25.0	SiO_2	-	.060	-
27	none	0.0	none	-	.097	-
28	IDP	10.0	SiO_2	-	.087	-
29	IDP	20.0	SiO_2	-	.070	-
30	IDP	30.0	SiO_2	-	.065	-
1	none	0.0	none	6	.091	.23
2	IDP	10.0	SiO_2	6	.081	.26
3	IDP	20.0	SiO_2	8	.067	.23
46-3	IDP	25.0	none	-	.063	.30
4	IDP	30.0	SiO_2	8	.057	.25
18A	DOZ	26.3	none	-	.050	.37
18	DOZ	26.3	none	-	.051	.28
19	DOZ	26.3	SiO_2	-	.062	.22
17-2	DOZ	25.0	MS	9	.069	.24
9	S-141	25.0	MS	8	.041	.350
10	S-141	25.0	SiO_2	8	.050	.34
17-3	S-141	25.0	MS	9	.061	.29
14	Ether 181	25.0	none	-	dissolved	
17-1	Oronite 6	25.0	MS	6	.075	.19
20	Light Circo Oil	22.9	MS	-	.074	.22
17-4	Light Circo Oil	25.0	none	6	.073	.27
46-2	Nujol	25.0	MS	-	.081	.23
46-1	Squalene	25.0	MS	-	.042	.42
7	Squalene	25.0	SiO_2	8	.044	.37
15	$C_{11}H_{23}CN$	25.0	none	-	.059	-
16	$C_{11}H_{23}CN$	25.0	SiO_2	-	.056	-

[a]Binder composition in Table XI.
[b]MS = contacted with Linde Molecular Sieves, SiO_2 = passed through column of silica gel.

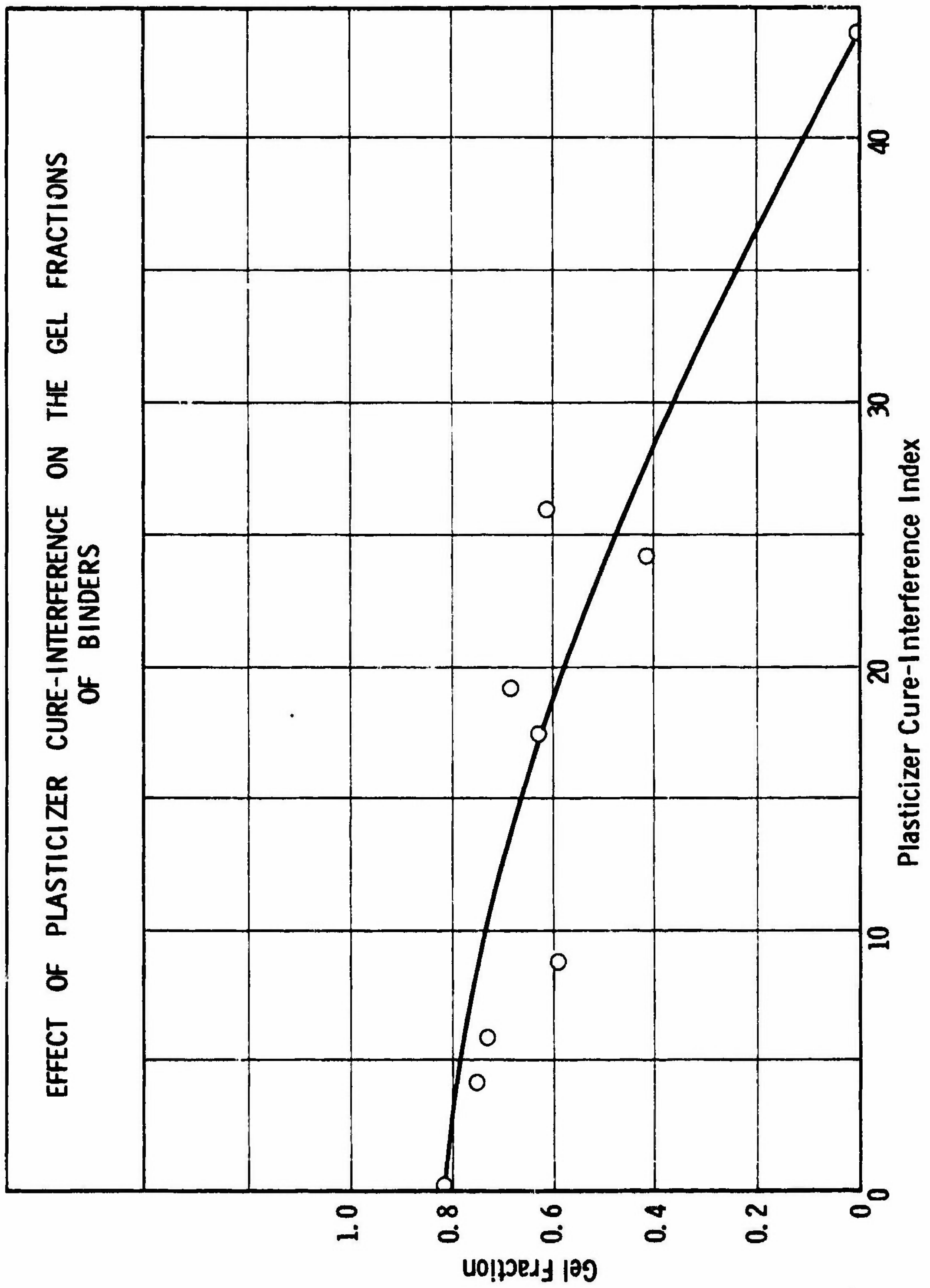

EFFECT OF PLASTICIZER CURE-INTERFERENCE ON THE GEL FRACTIONS OF BINDERS
Gel Fraction
1.0
0.8
0.6
0.4
0.2
0
Plasticizer Cure-Interference Index
0
10
20
30
40

Figure 9

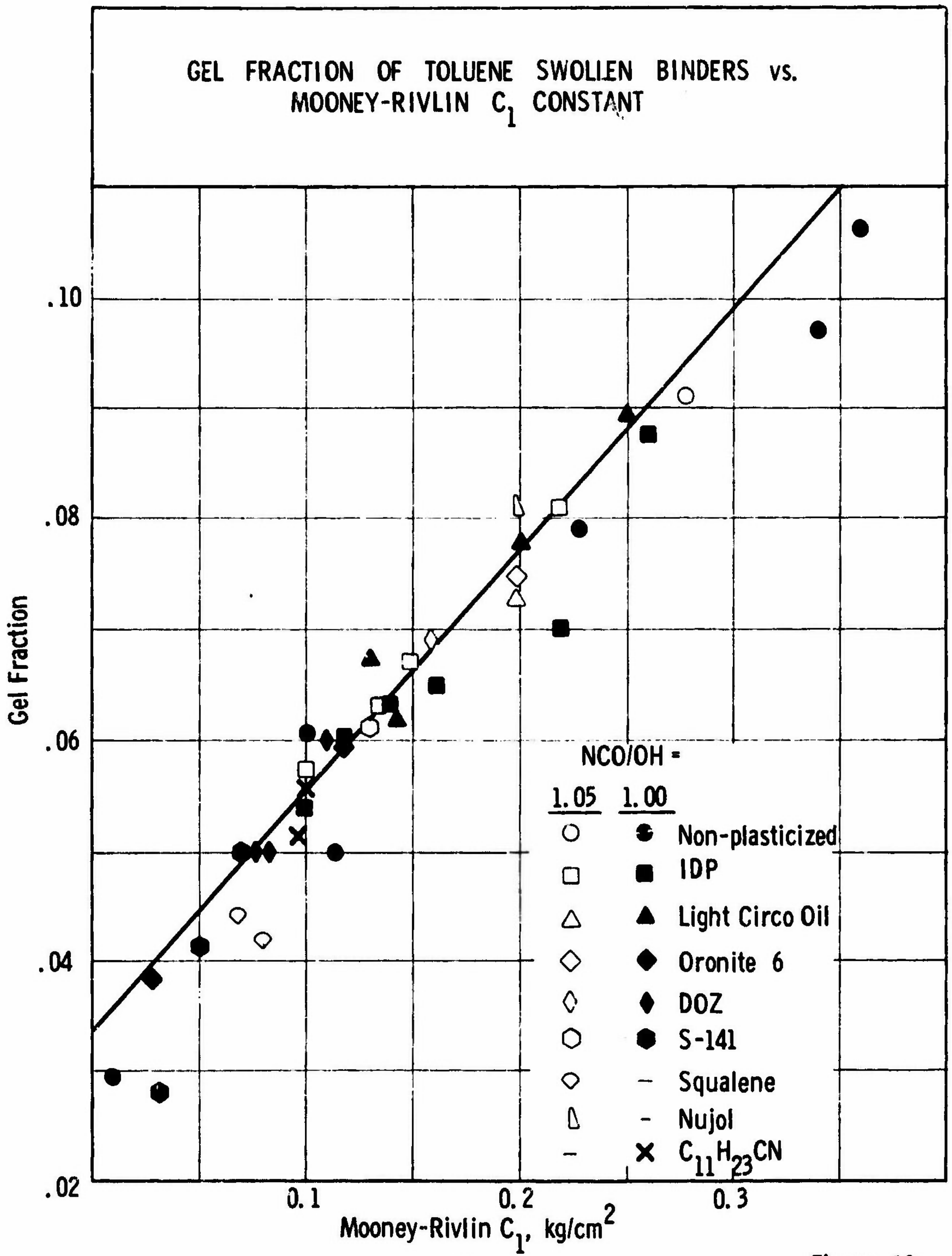

GEL FRACTION OF TOLUENE SWOLLEN BINDERS vs. MOONEY-RIVLIN C1 CONSTANT
Gel Fraction
.10
.08
.06
.04
.02
0.1
0.2
0.3
Mooney-Rivlin C1, kg/cm2
NCO/OH =
1.05
1.00
Non-plasticized
IDP
Light Circo Oil
Oronite 6
DOZ
S-141
Squalene
Nujol
C11H23CN

Figure 10

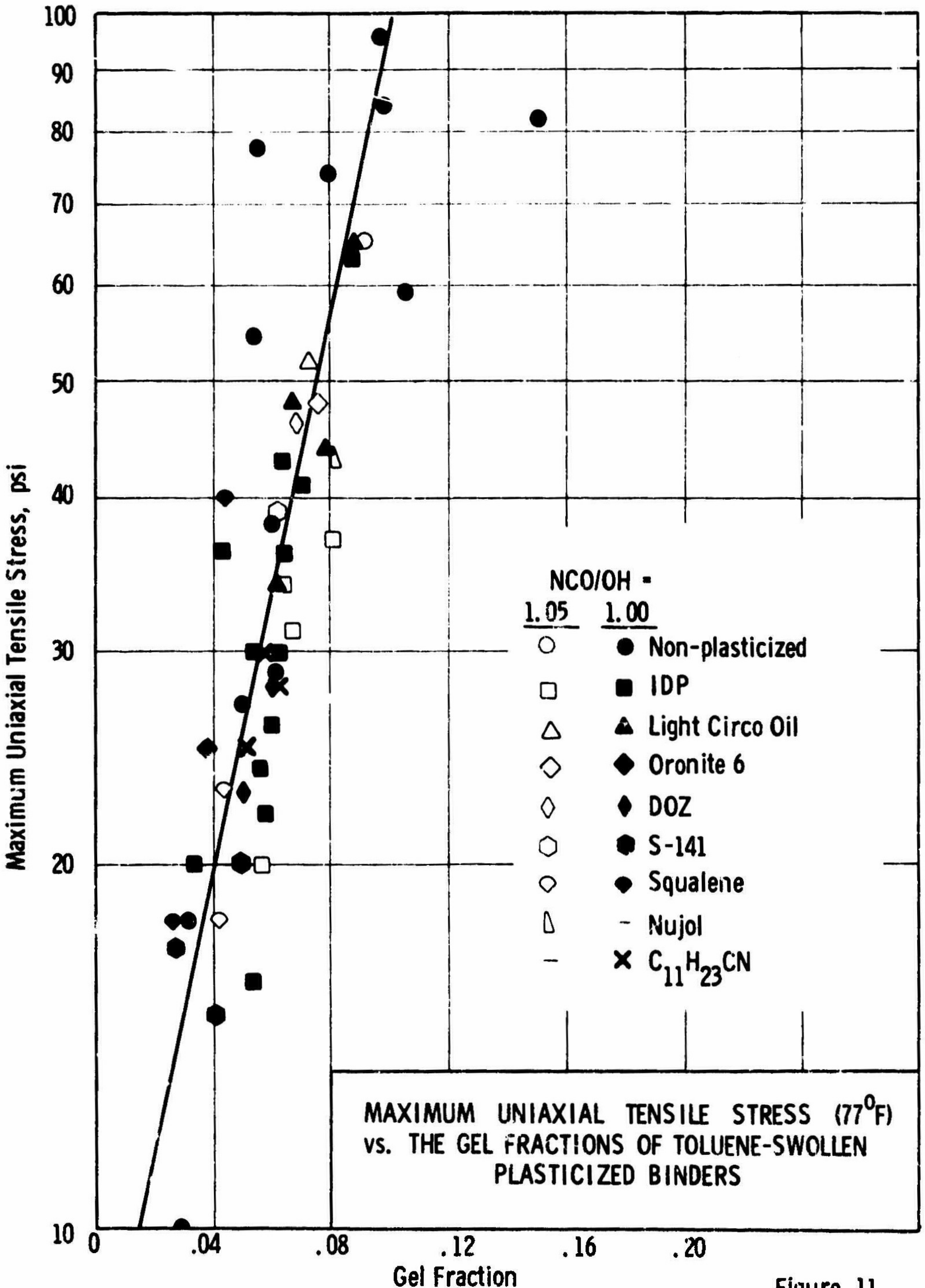

100
90
80
70
60
50
40
30
20
10
Maximum Uniaxial Tensile Stress, psi
0
.04
.08
.12
.16
.20
Gel Fraction
NCO/OH =
1.05 1.00
Non-plasticized
IDP
Light Circo Oil
Oronite 6
DOZ
S-141
Squalene
Nujol
$C_{11}H_{23}CN$
MAXIMUM UNIAXIAL TENSILE STRESS (77°F) vs. THE GEL FRACTIONS OF TOLUENE-SWOLLEN PLASTICIZED BINDERS

Figure 11

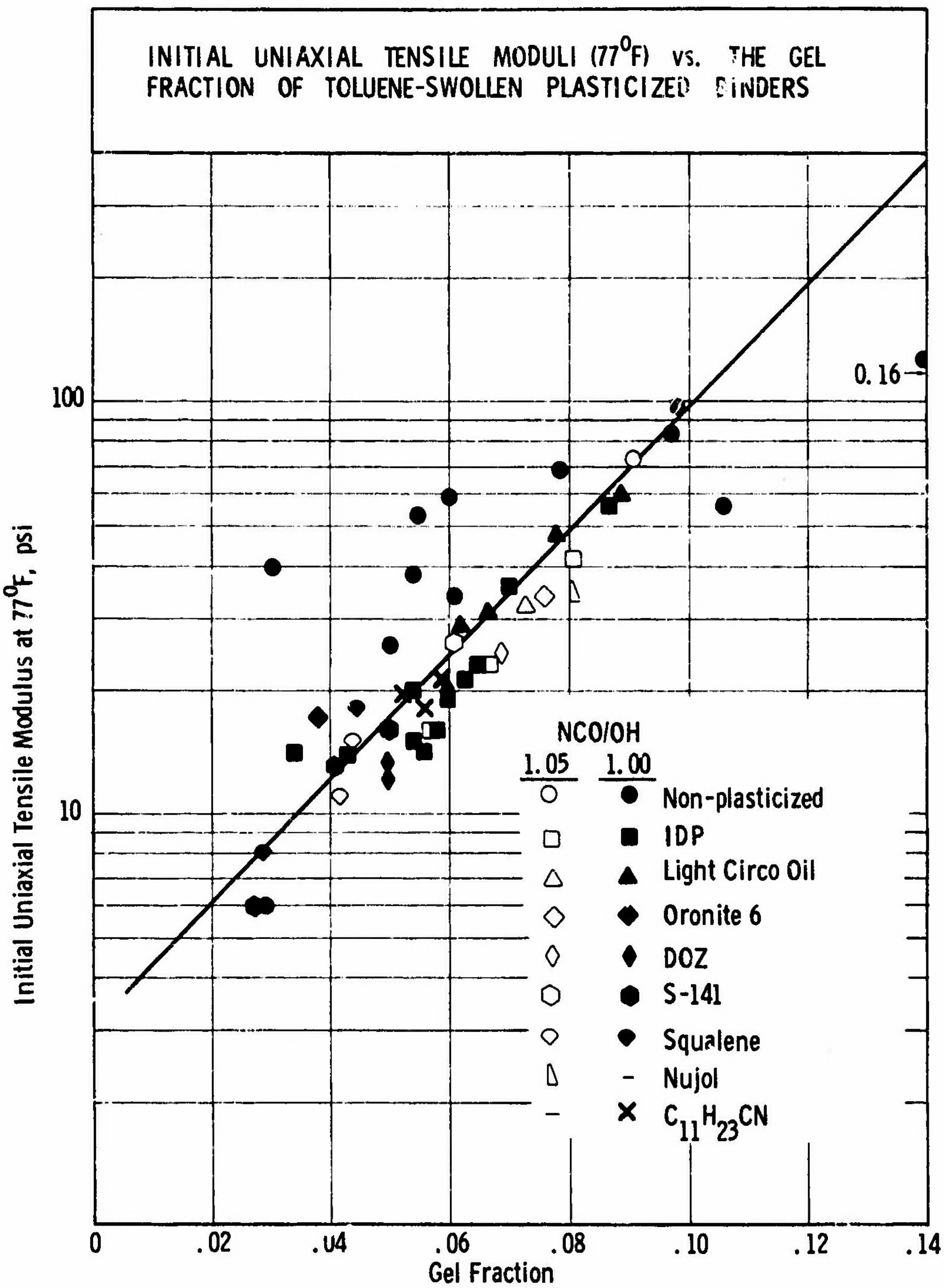

INITIAL UNIAXIAL TENSILE MODULI (77°F) vs. THE GEL FRACTION OF TOLUENE-SWOLLEN PLASTICIZED BINDERS
Initial Uniaxial Tensile Modulus at 77°F, psi
100
10
0.16
Gel Fraction
0
.02
.04
.06
.08
.10
.12
.14
NCO/OH
1.05
1.00
Non-plasticized
IDP
Light Circo Oil
Oronite 6
DOZ
S-141
Squalene
Nujol
$C_{11}H_{23}CN$

Figure 12

Table XVIII

EFFECT OF PLASTICIZER CURE-INTERFERENCE ON GEL FRACTION OF BINDERS (U)

Plasticizer	Cure-Interference Index[a]	Rate of Isocyanate Reaction	Gel Fraction
None	0.0	-	0.091
Nujol	0.1	fast	0.081
Oronite 6	4.2	fast	0.075
Light Circo Oil	5.9	fast	0.073
IDP	17.7	moderate	0.063
DOZ	19.2	moderate	0.069
Squalene	24.2	no data	0.042
S-141	26.0	no data	0.061
Ansul Ether 181	44.9	slow	dissolves

[a]See Table V.

(U) Figures 13 through 18 show the effect of plasticizer content and treatment on the gel fraction of toluene swollen binders. Figures 14, 15 and 18 suggest that the gel fraction varies linearly with the plasticizer content. These figures also suggest that passing the IDP and DOZ through a column of silica gel was a more effective treatment than drying over molecular sieves. The hydrocarbon plasticizers, except squalene, were not much affected by treatment probably because they contained very little contaminants which interfere with cure. Squalene and S-141 were not greatly improved by treatment with silica gel or molecular sieves.

5) Mechanical Properties at Low-Temperature (U)

(U) The workhorse binder was a highly successful binder in many applications, but its properties at low temperature were disappointing. The effort to improve the low temperature properties with plasticization was not successful. There were two obvious causes which could be responsible for poor low temperature behavior: a high glass transition temperature and crystallization of the polymer. Both of these were investigated during the previous program[1], and the data indicated that neither were the cause.

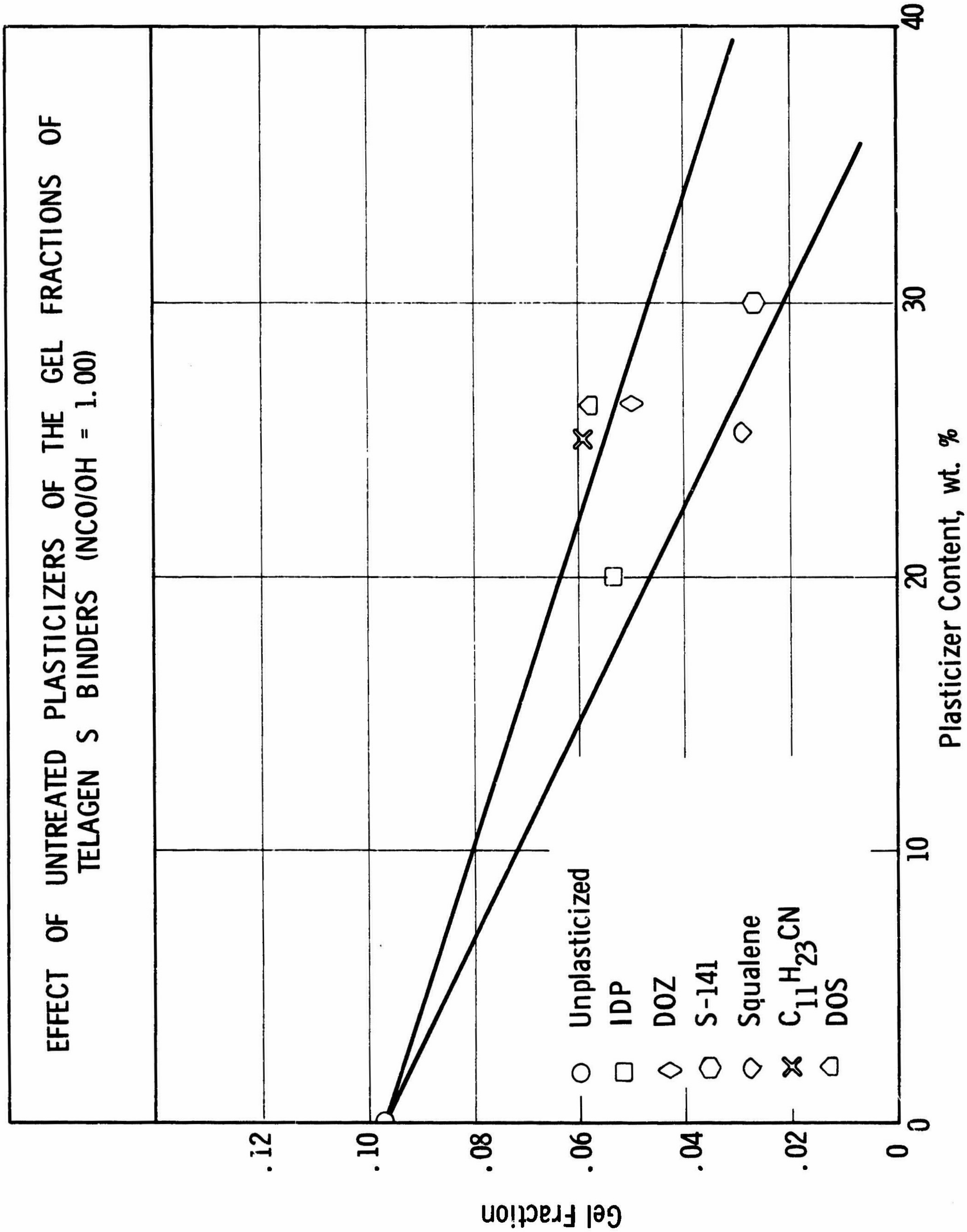

EFFECT OF UNTREATED PLASTICIZERS OF THE GEL FRACTIONS OF TELAGEN S BINDERS (NCO/OH = 1.00)
Unplasticized
IDP
DOZ
S-141
Squalene
C11H23CN
DOS
Gel Fraction
.12
.10
.08
.06
.04
.02
0
Plasticizer Content, wt. %
0
10
20
30
40

Figure 13

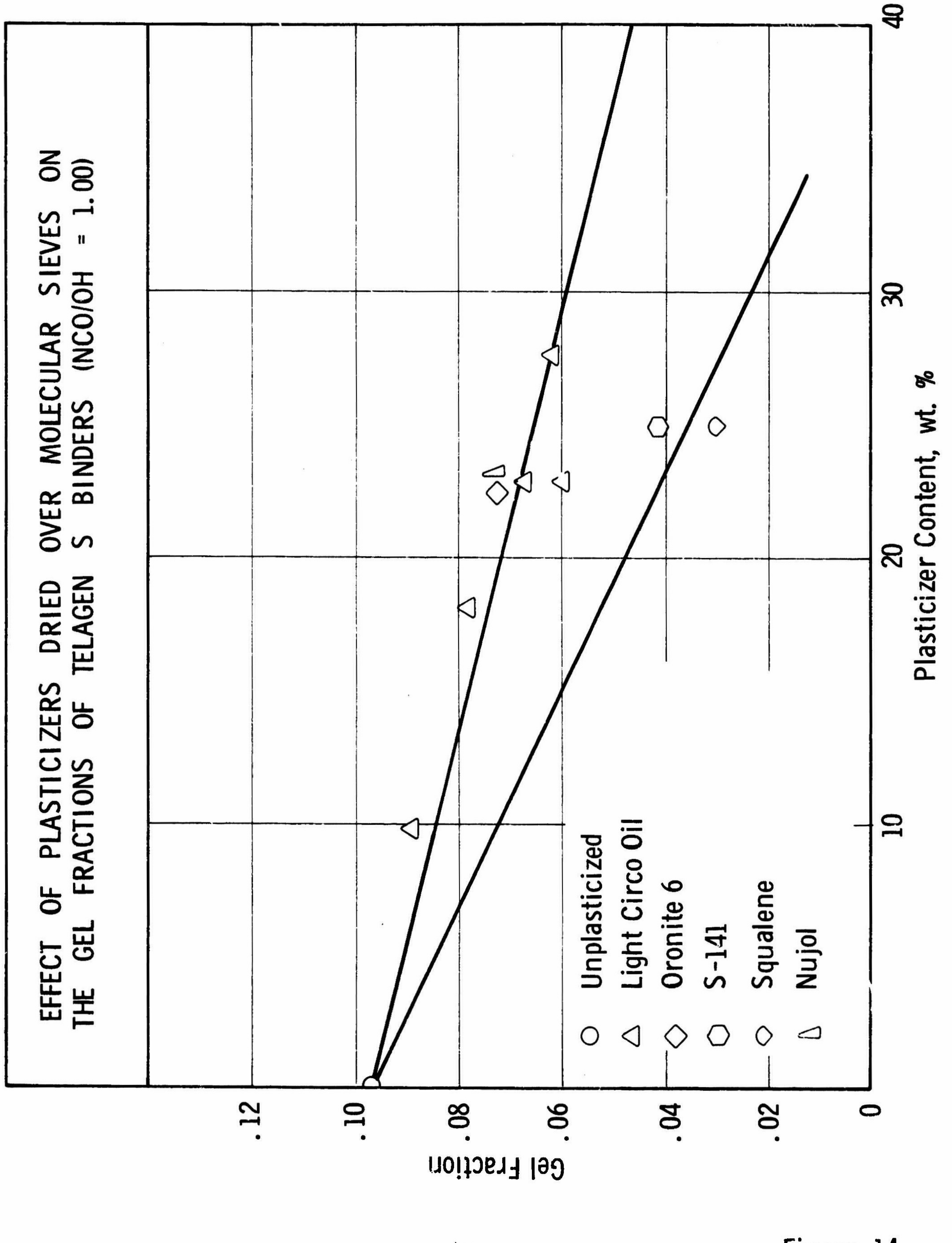

EFFECT OF PLASTICIZERS DRIED OVER MOLECULAR SIEVES ON
THE GEL FRACTIONS OF TELAGEN S BINDERS (NCO/OH = 1.00)
Unplasticized
Light Circo Oil
Oronite 6
S-141
Squalene
Nujol
Gel Fraction
.12
.10
.08
.06
.04
.02
0
10
20
30
40
Plasticizer Content, wt. %

Figure 14

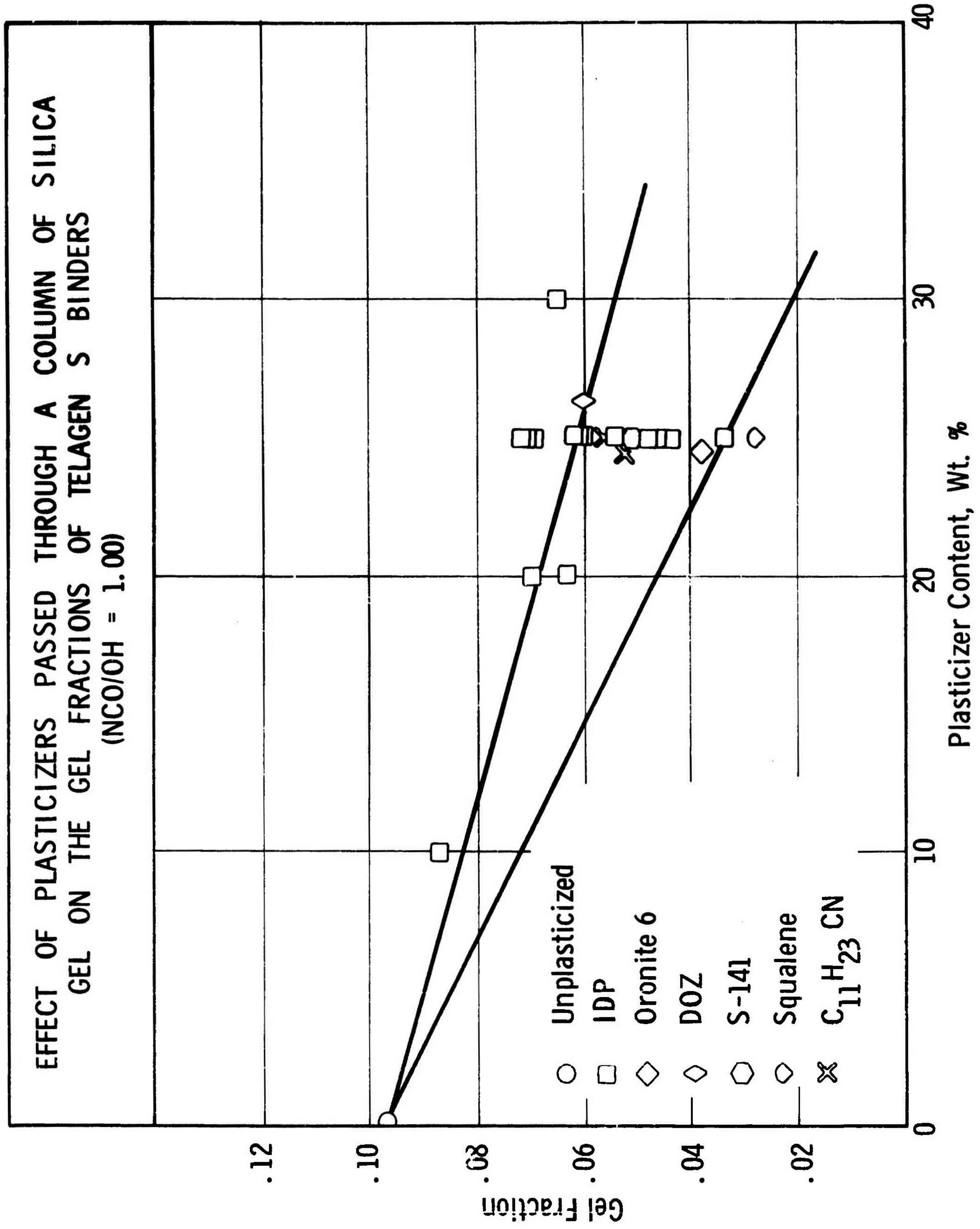

EFFECT OF PLASTICIZERS PASSED THROUGH A COLUMN OF SILICA GEL ON THE GEL FRACTIONS OF TELAGEN S BINDERS
(NCO/OH = 1.00)
Unplasticized
IDP
Oronite 6
DOZ
S-141
Squalene
$C_{11}H_{23}CN$
Gel Fraction
.12
.10
.08
.06
.04
.02
0
10
20
30
40
Plasticizer Content, Wt. %

Figure 15

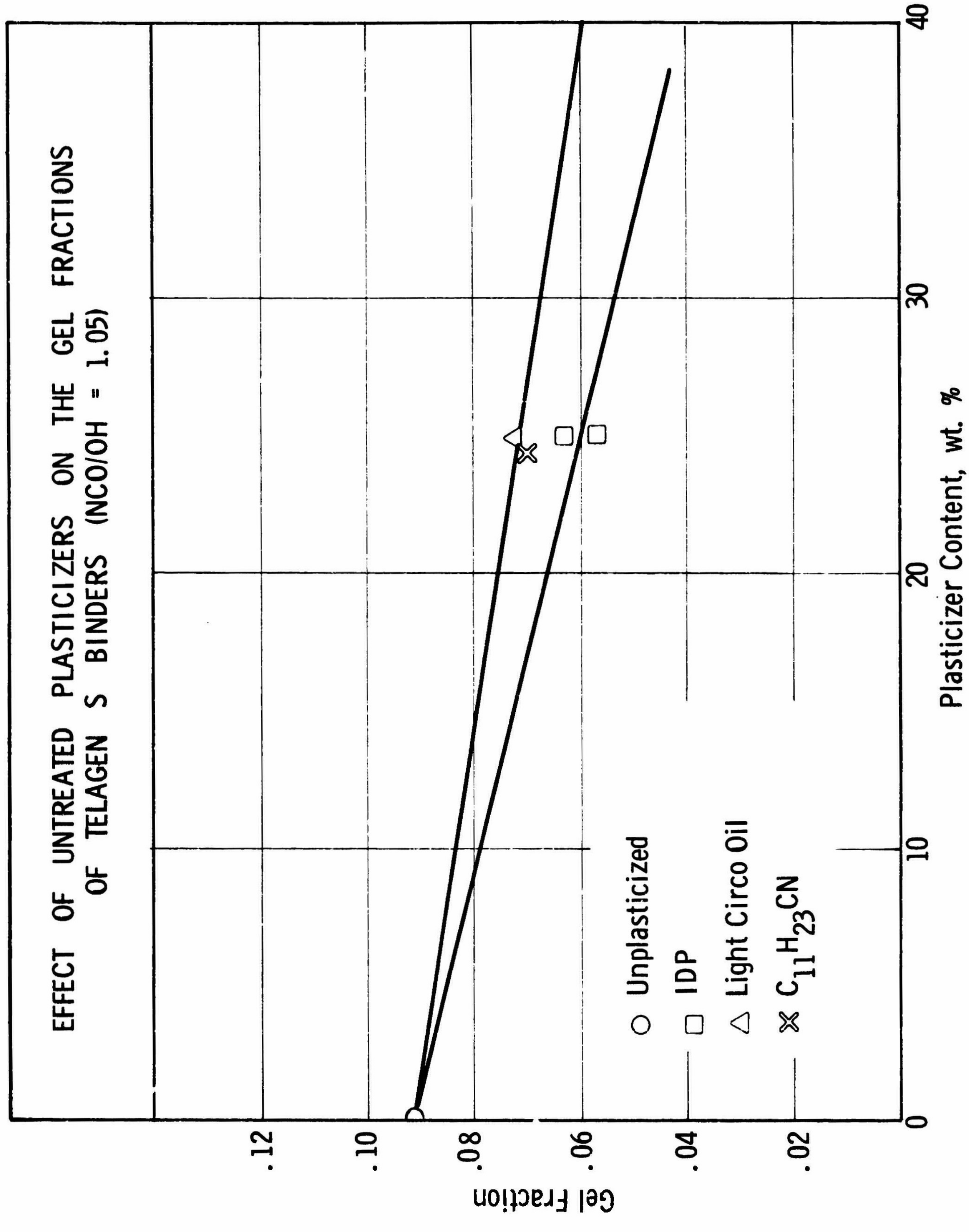
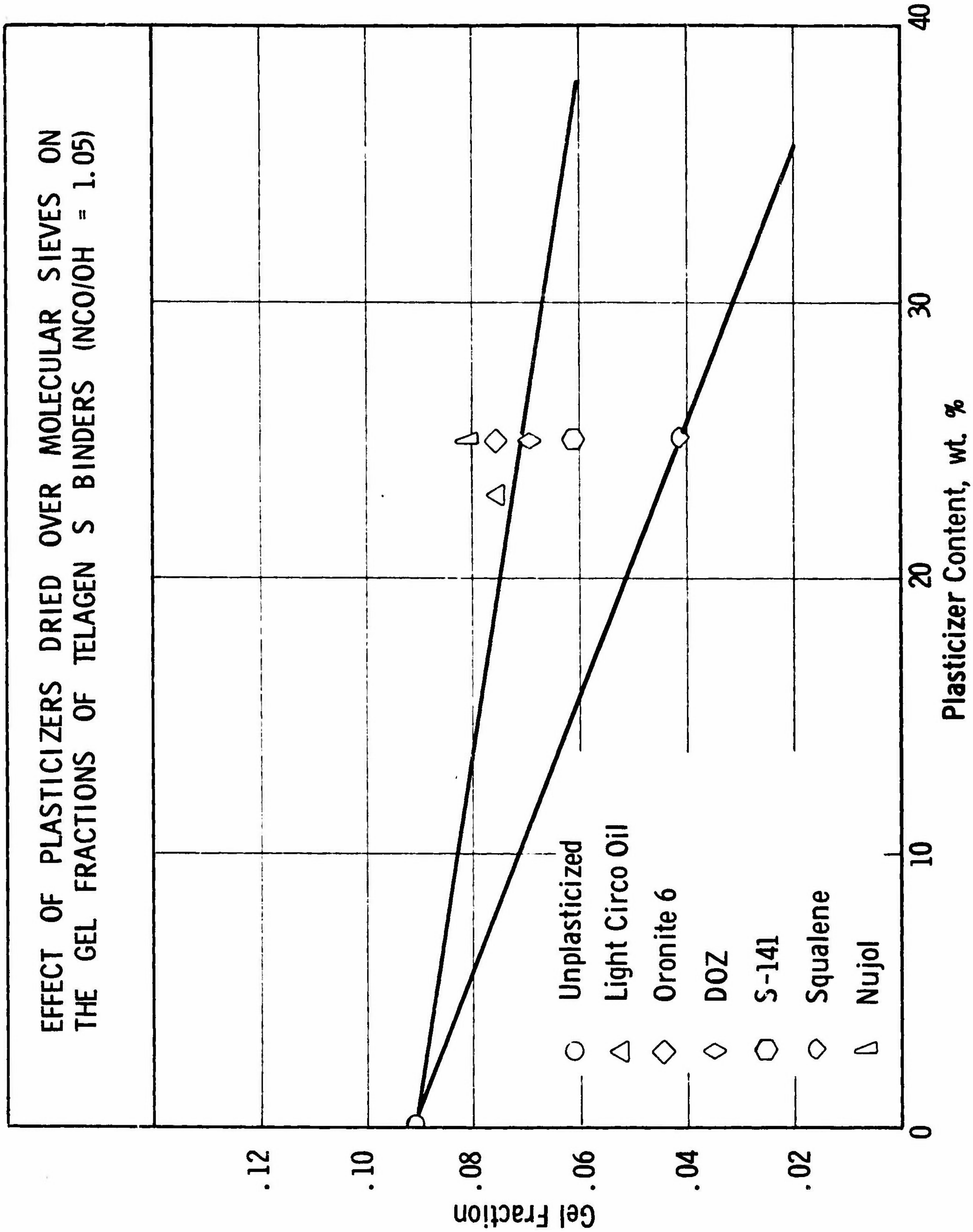

EFFECT OF UNTREATED PLASTICIZERS ON THE GEL FRACTIONS
OF TELAGEN S BINDERS (NCO/OH = 1.05)
Unplasticized
IDP
Light Circo Oil
$C_{11}H_{23}CN$
Gel Fraction
.12
.10
.08
.06
.04
.02
Plasticizer Content, wt. %
0
10
20
30
40

Figure 16



EFFECT OF PLASTICIZERS DRIED OVER MOLECULAR SIEVES ON THE GEL FRACTIONS OF TELAGEN S BINDERS (NCO/OH = 1.05)
Unplasticized
Light Circo Oil
Oronite 6
DOZ
S-141
Squalene
Nujol
Gel Fraction
.12
.10
.08
.06
.04
.02
0
10
20
30
40
Plasticizer Content, wt. %

Figure 17

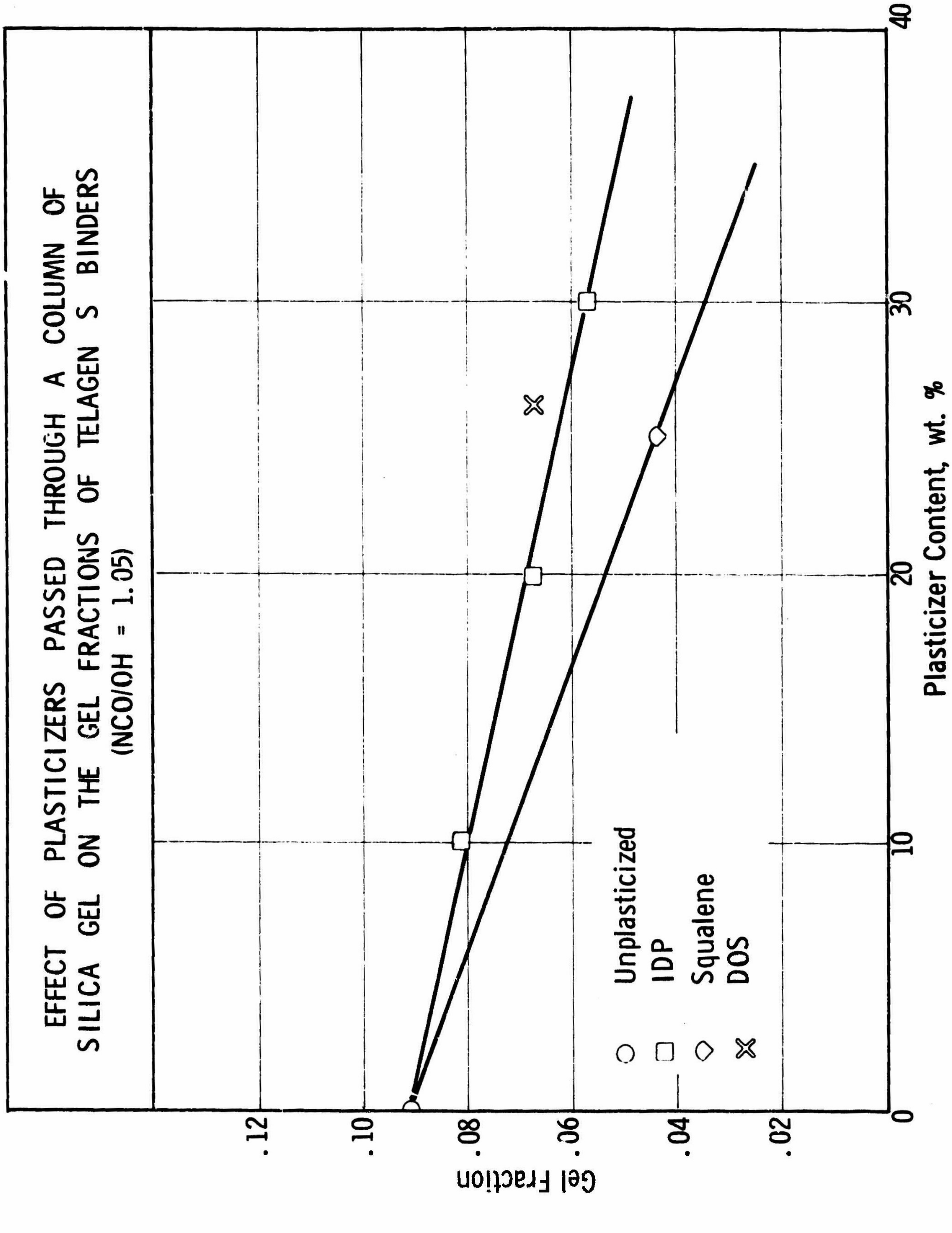

EFFECT OF PLASTICIZERS PASSED THROUGH A COLUMN OF SILICA GEL ON THE GEL FRACTIONS OF TELAGEN S BINDERS
(NCO/OH = 1.05)
○ Unplasticized
□ IDP
◇ Squalene
⊠ DOS
Gel Fraction
.12
.10
.08
.06
.04
.02
0
10
20
30
40
Plasticizer Content, wt. %

Figure 18

(U) Investigations of the effect of plasticizers on low temperature properties were made. These studies involved glass transition temperature, low temperature mechanical behavior, and effect of temperature and plasticizers on the NMR band widths.

(U) Table XIX indicates the glass transition temperature (by density measurement) of plasticized Telagen S binders. The variation of T_G with the plasticizer was minor and in all cases the T_G was low enough to exclude it as a cause for poor low temperature properties.

Table XIX

EFFECT OF PLASTICIZER ON T_G OF TELAGEN S BINDER (U)

Plasticizer[a]	T_G °F	T_G °C
Oronite 6	-121	-85
DOZ	-125	-87
S-141	-121	-85
Light Circo Oil	-112	-80

[a] 25% by weight

(U) Table XX shows how the plasticizers actually affect low temperature mechanical behavior of the binder. A cursory look at the low temperature moduli seemed to indicate that plasticizers did measurably improve the low temperature moduli. That this was not so, is demonstrated by Figure 19 which shows that the initial moduli at -40 and -75°F are a function of the initial moduli at 77°F. Thus the plasticizer did not cause the improved low temperature moduli as the low modulus at low temperatures could have been attained by preparing non-plasticized binders with lower crosslink densities.

(U) A good low-temperature propellant would have a modulus of about 10,000 psi at -75°F. The binders shown in Table XX would have moduli of from 10^6 to 10^7 at -75°F if they were loaded with 88 wt% solids.

(U) Wide-line NMR has also been used as a technique for measuring glass transition temperatures of polymers[6]. Work along these lines has been done at Aerojet[2]. The width of the NMR absorption band is strongly dependent upon the mobility of the protons in the sample; with a decrease of proton mobility, the line width increases. Thus, a plot of line width against temperature gives a curve with two breaks. One break shows the glass transition temperature and the other is due to the limit of the instrument. The data for the uncured prepolymer and plasticized binders are shown in Table XXI and Figures 20-22. The non-plasticized binder showed the highest T_G and of the plasticized binders that containing IDP had the lowest T_G. The gel

Table XX

EFFECT OF PLASTICIZERS ON LOW TEMPERATURE MECHANICAL PROPERTIES (U)

Reference No.	Plasticizer	Content Wt%	Mechanical Properties 77°F σ_m	77°F ϵ_m	77°F ϵ_b	77°F E_o	-40°F σ_m	-40°F ϵ_m	-40°F ϵ_b	-40°F E_o	-75°F σ_m	-75°F ϵ_m	-75°F ϵ_b	-75°F E_o
1	None	0	65	358	358	72	1805	192	192	3600	3570	7	176[c]	75000
2	IDP	10	37	325	325	41	749	266	266	930	3160	210	216	30500
3	IDP	20	31	375	375	23	440	317	317	410	1390	210	210	1250
4	IDP	30	20	365	365	16	340	440	440	270	1130	240	246	900
17-2	DOZ	25	46	472	472	24	786	447	447	380	1000[b]	225[b]	225	1140
17-3	S-141	25	39	506	506	26	897	277	278	740	1490	165	165	1697
17-4	Light Circo Oil	25	52	404	404	32	936	270	271	880	2930	215	215	13360
17-1	Oronite 6	25	48	400	400	34	976	324	326	780	1161	187	187	1238

[a]For binder composition see Table XI.
[b]Break at flaw.
[c]Yield point.

INITIAL TENSILE MODULUS AT 77^{0}F vs. INITIAL TENSILE MODULUS AT -75^{0}F FOR PLASTICIZED TELAGEN S BINDERS

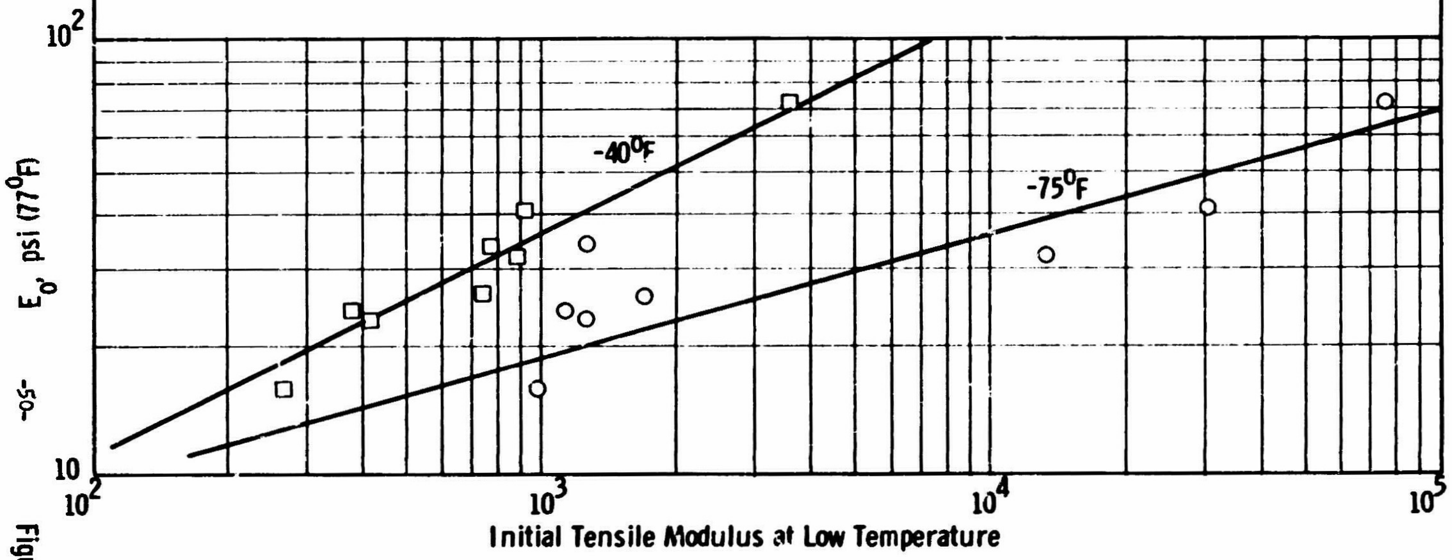


Figure 19

NMR LINE WIDTH vs. TEMPERATURE FOR TELAGEN S PREPOLYMER AND NON-PLASTICIZED BINDER

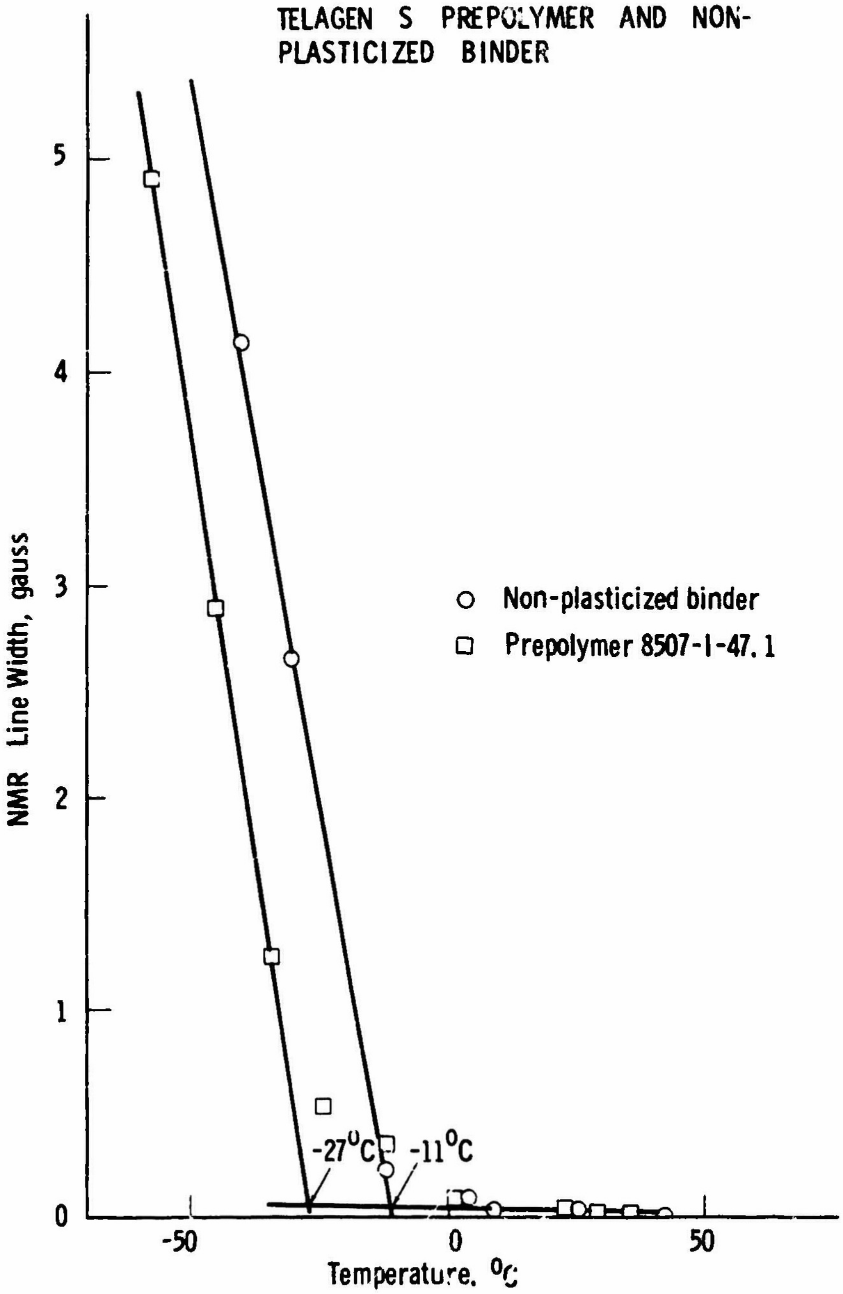


Figure 20

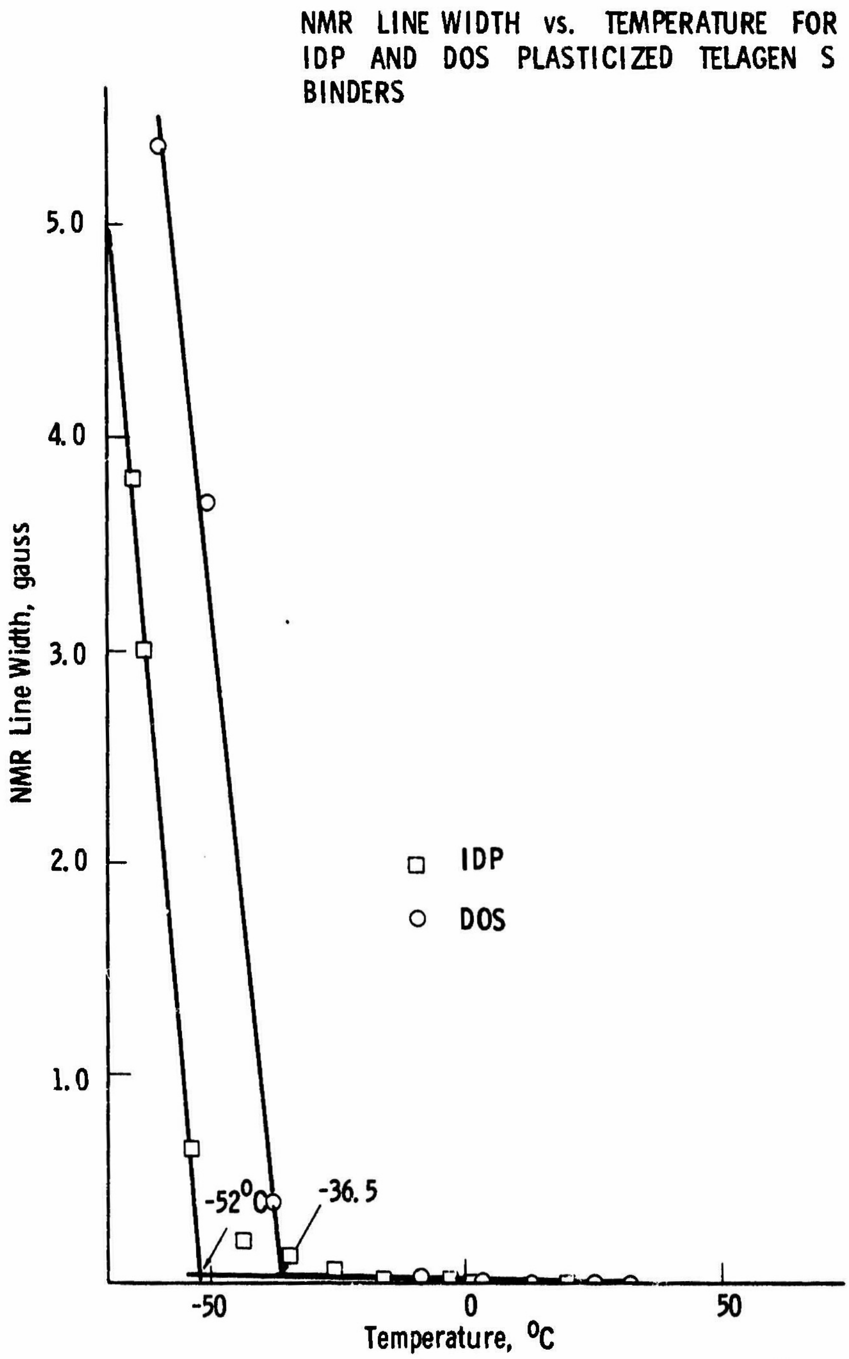

NMR LINE WIDTH vs. TEMPERATURE FOR IDP AND DOS PLASTICIZED TELAGEN S BINDERS
5.0
4.0
3.0
2.0
1.0
NMR Line Width, gauss
IDP
DOS
-52°C
-36.5
-50
0
50
Temperature, °C

Figure 21

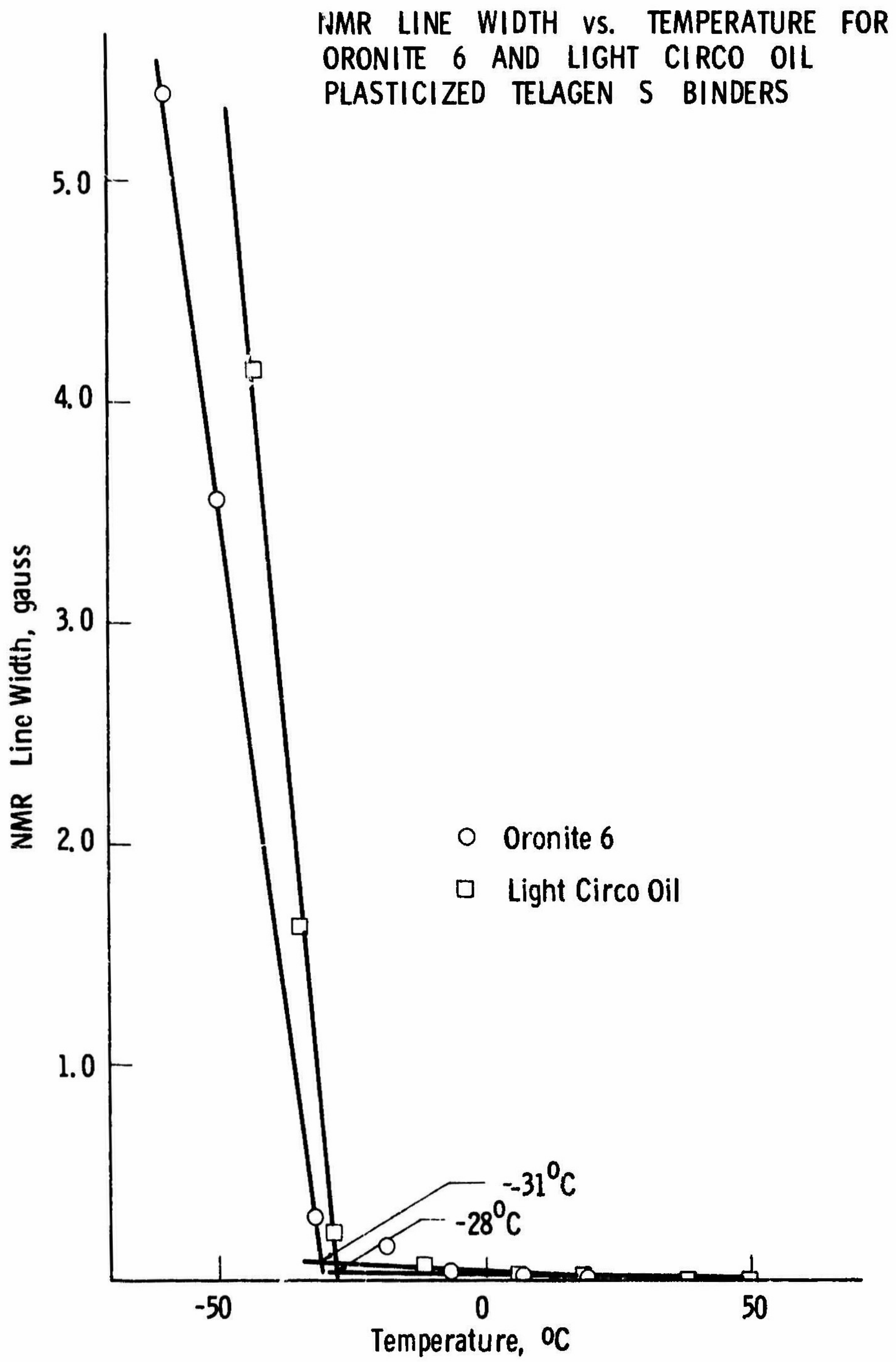
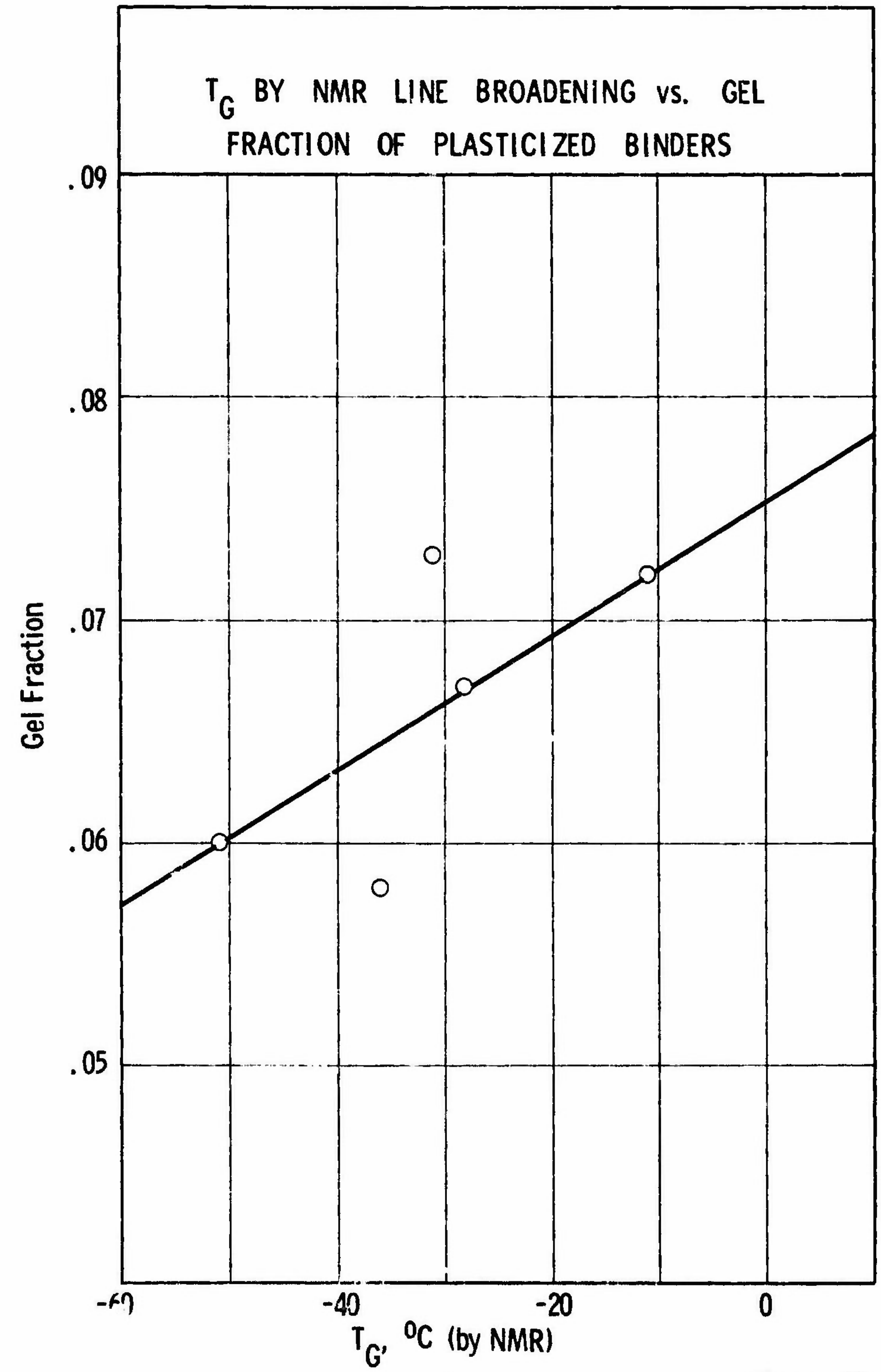

NMR LINE WIDTH vs. TEMPERATURE FOR ORONITE 6 AND LIGHT CIRCO OIL PLASTICIZED TELAGEN S BINDERS
5.0
4.0
3.0
2.0
1.0
NMR Line Width, gauss
Oronite 6
Light Circo Oil
-31°C
-28°C
-50
0
50
Temperature, °C

Figure 22



T_G BY NMR LINE BROADENING vs. GEL FRACTION OF PLASTICIZED BINDERS
.09
.08
.07
.06
.05
Gel Fraction
-40
-20
0
T_G, °C (by NMR)

Figure 23

fraction of the binders in Table XXI showed a correlation with the T_G by NMR line broadening (Figure 23). This cast some doubt on the validity of this application of NMR line width for determining T_G. Apparently the line broadening is due to restriction of proton motion by the formation of a network. The transition observed in the line width-temperature plot apparently reflects the temperature at which the proton reaches a critical restriction and this temperature is a function of the density of the network rather than a function of the plasticizer. While there are valid doubts that the observed transitions are glass transitions, they may be related to low temperature mechanical behavior.

Table XXI

GLASS TRANSITION TEMPERATURE BY NMR LINE BROADENING (U)

Reference No.[a]	Plasticizer[b]	T_G, °C	Gel Fraction
Prepolymer 8507-I-47.1	none	-27	-
45	none	-11	0.072
20	Light Circo Oil	-28	0.067
42	Oronite 6	-31	0.073
37	DOS	-36	0.058
17C	IDP	-52	0.060

[a]Binder composition, Table XI.
[b]26 vol %.

6) Compatibility of Plasticizers with Telagen S Binders (U)

(U) Some visual observations of plasticizer (26 vol %) compatibility with the Telagen S-CTI-HDI binders were made. S-141-plasticized binders tended to exude; the exudate was presumed to be plasticizer. The binder containing Oronite 6 was cloudy, whereas the binders with Nujol and Circo Oil were slightly hazy. The clearest binder was one with IDP.

7) Conclusions (U)

(U) The experimental study of plasticized binders definitely demonstrated an interference by the plasticizers with the curing reactions. The cure-interference was minor for hydrocarbon type plasticizers such as Nujol, Light Circo Oil, and Oronite 6, moderate for esters such as IDP, DOS, and DOZ, and pronounced for squalene, S-141, and Ansul Ether 181. The extent of cure-interference was generally decreased by purification of the plasticizer.

(U) Even with plasticizers which did not interfere with the cure, a binder cured with a plasticizer showed a lower crosslink density than a binder cured without plasticizer. Evidence also indicated that the plasticizing effect of the plasticizer did not exist, but that it was the result of a lower crosslink density. These results cast a doubt as to the value of plasticizers in the systems studied.

e. Binders Containing New Curing Agents (U)

1) Reduced Toluene Diisocyanate (RTDI) (U)

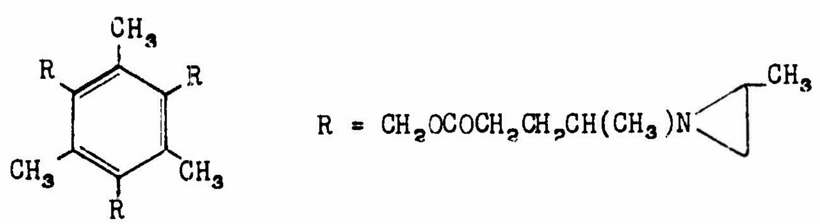
(U) Reduced toluene diisocyanate (RTDI) and toluene diisocyanate (TDI) were used as chain extenders in Binders 60-63 and 96-97 (Table XI). Binders containing TDI or HDI showed similar gel fractions while those made with RTDI had lower gel fractions. RTDI, obtained from the Union Carbide Corp., was a saturated analog of TDI and labeled "all pure R-TDI isomers". The analyses were listed as follows:

Purity by amine titration	96.28%
Hydrolyzable chlorides	0.026%
Total chlorides	0.04%

(U) RTDI was not an effective replacement for HDI. This conclusion was supported by data in Table XI. For instance, compare the mechanical properties, crosslink density and gel fraction of Binder 96 with those of Binders 100 and 102; or compare the same parameters for Binder 97 with those of Binders 87, 101, and 103. It is true that the properties of Binder 96 are at least the equivalent of those of Binder 77, but the majority of the data indicated that RTDI was not as good a curing agent as HDI.

2) Aziridine C-100 (U)

(U) An aziridine curing agent, C-100, was supplied by the American Cyanamid Company and was reported to cure at room temperature. The aziridine was 1,3,5-trimethyl-2,4,6-tri-[3-(2-methylaziridinyl-1)butyroxymethyl]benzene (aziridine assay = 95%). The results of experiments with the product are listed in Table XXII. All of these binders were cured at 135°F for 10 days, and no attempts to cure at room temperature were made.



C-100

(U) Apparently, C-100 reacted as efficiently with Prepolymer 148D as with Prepolymer 148DH-3. The gel fractions were different, but Prepolymer 148D, unsaturated carboxy terminated prepolymer, had an equivalent weight of 985 and its saturated counterpart, Prepolymer 148DH-3, had an equivalent weight of 1120. Comparison of Binder 51 in Table XI with Binder 69 in Table XI indicated that the isocyanates were the better curing agents.

Table XXII

EFFECT OF PLASTICIZERS ON THE GEL FRACTION OF HYDROCARBON BINDERS[a] CURED WITH THE AZIRIDINE C-100 (U)

Reference No.	Plasticizer	% Wt.	Plasticizer[b] Treatment	Cure Time, days at 135°F	Gel Fraction
64	Arneel OD	25	none	10	0.136
65	IDP	25	SiO	10	0.133
66	none	-	-	10	0.189
67	Arneel OD	25	none	10	0.112
68	IDP	25	SiO_2	10	0.128
69	none	-	-	10	0.152

[a]Carboxy-terminated hydrocarbon prepolymers, Binders 64-66, Lot 148D unsaturated and Binders 67-69, Lot 148DH-3 saturated, at aziridine to acid ratio of 1 to 1.
[b]SiO_2 = passed through a column of silica gel.

(U) The results of using IDP or Arneel OD with C-100 binders indicated that both of these plasticizers changed the crosslink density. It is apparent then that the isocyanates are not the only curing agents subject to interference by plasticizers.

f. Binders Containing C-1 (U)

(U) The bonding agent, C-1, was incorporated into binder formulations to simulate more closely propellant binder. The gel fractions of these binders did not indicate any interference with the extent of cure. Compare gel fractions of Binders 17-4 and 58.

g. Solvent Swelling (U)

(U) Under Contract AF 04(611)-10386 the swelling of binders and propellants was done exclusively with ethylene dichloride. There were many indications that this was not the best solvent for the isocyanate cured

system which was developed. A further study of swelling solvents was initiated as part of the current contract.

(U) A primary hydroxyl terminated Telagen S cured with a combination of CTI and HDI (theoretical crosslink density: 0.5×10^{-4} moles of crosslinker per gram of binder) was swollen in nitromethane, tetrahydrofuran, dioxane, chloroform, benzene, cyclohexane, n-hexane, methyl ethyl ketone, ethyl acetate, n-heptane, toluene, acetonitrile, and ethylene dichloride. Figure 24 shows the degree of swelling with time.

(U) Although there are a few exceptions, most of the solvents achieved the maximum swelling in about seven days. Tetrahydrofuran reaches the maximum in about 3 days while dioxane was still increasing on the tenth day. After reaching the maximum, the swelling decreased slowly. The solvents continued to extract soluble material, but this extractable material did not account for the decrease in swelling.

(U) Figure 25 indicates the relation between the maximum swelling for various solvents and the cohesive energy density (CED) of the solvent. The solvents and their cohesive energy densities are given in Table XXIII. The data are scattered but there is definitely greater swelling by solvents with CED's of from 70 to 90. The curve gives 77 as the CED of the elastomer, but this value depends on how the curve is drawn. Certainly though, the CED of elastomer is close to 80.

(U) Swelling of binder samples with the cyanide-type plasticizers gave erroneously high gel fractions because the extracted plasticizer was evaporating with the swelling solvent (toluene) during isolation of the extractables. The weight of extractables was therefore determined from the difference in the weights of the original sample and the deswollen sample (solvent removed in vacuo). This method gave more reliable values for the extractables in the cyanide-plasticized binders. Several of the swollen binders with other types of plasticizers were deswollen and the amounts of extractables determined by this method. In most cases, the amount of extractables by this method agreed within 5% or less with that determined by weight of non-volatiles in the swelling solvents.

(U) Samples of a non-plasticized binder of known crosslink density were placed in several plasticizers and their swelling characteristics determined. Of these plasticizers, IDP, n-undecyl cyanide and squalene cause the more rapid swelling; the other plasticizers studied include, DOS, Light Circo Oil, Oronite 6 and Nujol.

(U) Figure 26 shows the gel fraction-crosslink density relation for Telagen S binders. The slope of the line is 1.95, greater than the theoretical 1.67, and yields a χ value of 0.497 for the toluene-Telagen S binder interaction.

h. Mooney-Rivlin Constants (U)

Mooney-Rivlin plots of many binder mechanical properties data were made and the values of the C_1 and C_2 constants were derived. These are shown in Table XI.

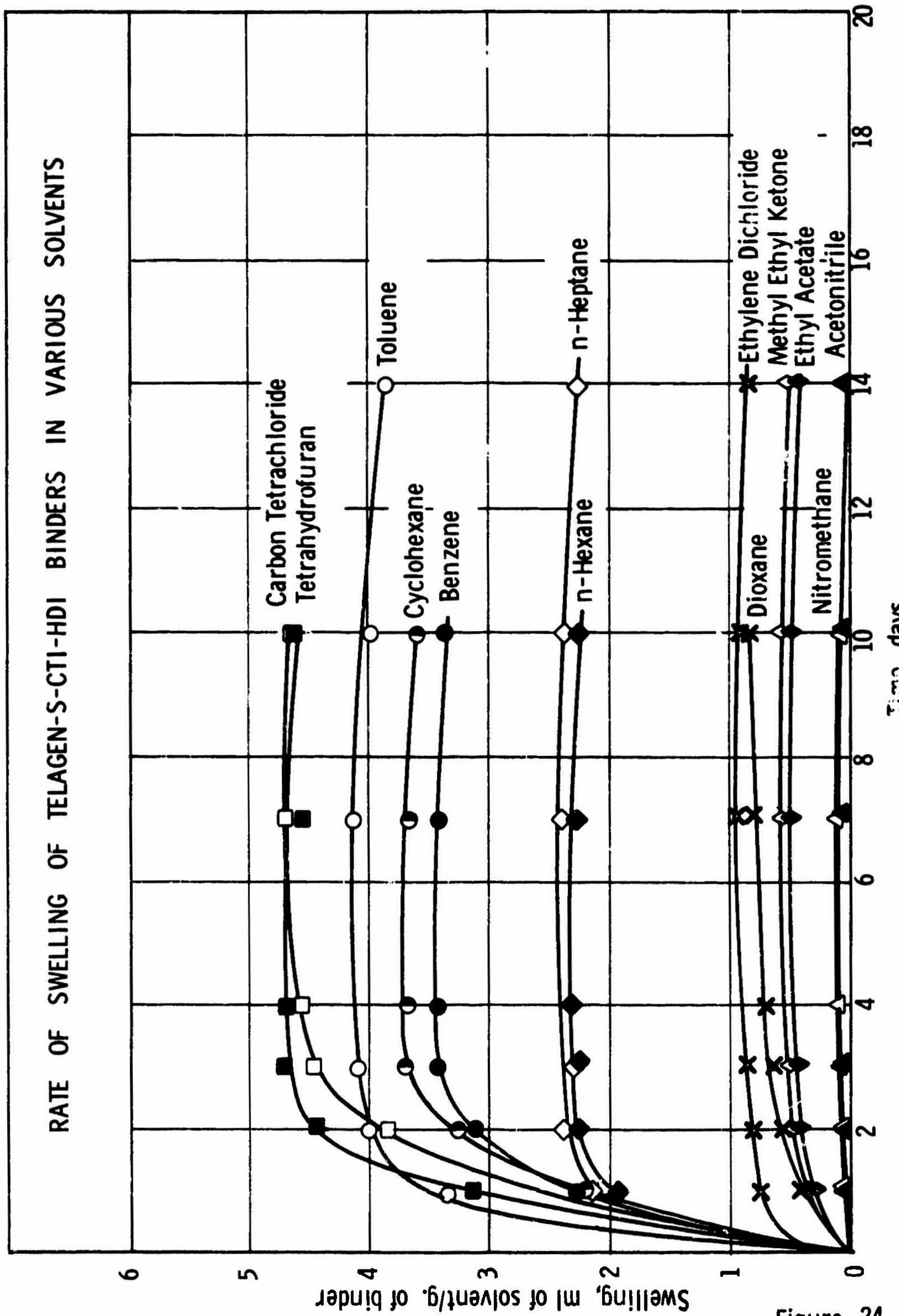

RATE OF SWELLING OF TELAGEN-S-CTI-HDI BINDERS IN VARIOUS SOLVENTS
Carbon Tetrachloride
Tetrahydrofuran
Toluene
Cyclohexane
Benzene
n-Heptane
n-Hexane
Ethylene Dichloride
Methyl Ethyl Ketone
Ethyl Acetate
Acetonitrile
Dioxane
Nitromethane
Swelling, ml of solvent/g. of binder
0
1
2
3
4
5
6
Time, days
2
4
6
8
10
12
14
16
18
20

Figure 24

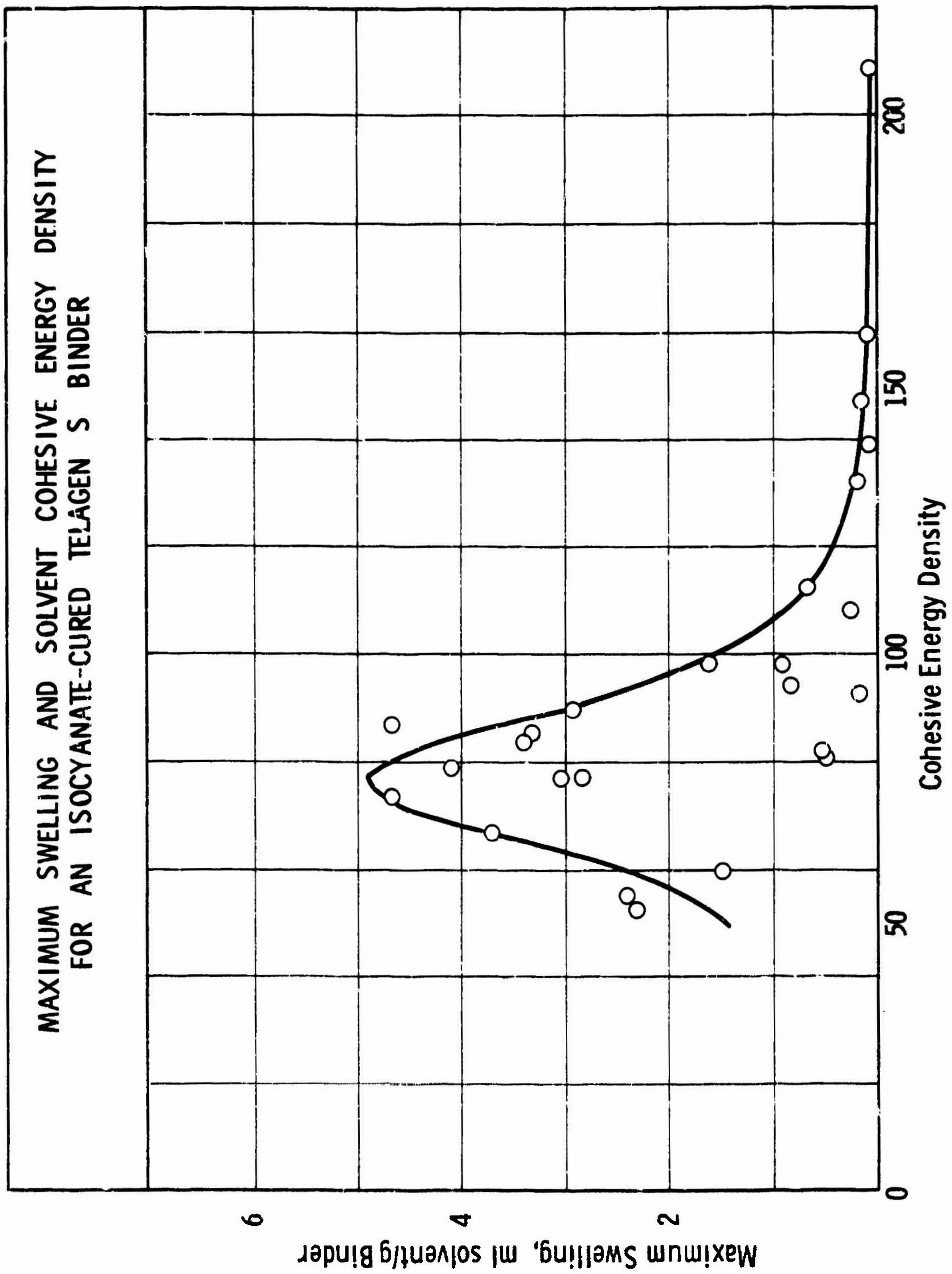

MAXIMUM SWELLING AND SOLVENT COHESIVE ENERGY DENSITY
FOR AN ISOCYANATE-CURED TELAGEN S BINDER
Cohesive Energy Density
0
50
100
150
200
Maximum Swelling, ml solvent/g Binder
2
4
6

Figure 25

Table XXIII

MAXIMUM SWELLING AND THE COHESIVE ENERGY DENSITIES (CED) OF SOLVENTS (U)

Solvent	CED	Maximum Swelling ml solvent/g binder
methanol	209	0.062
Nitromethane	159	0.11
Dimethylformamide	147	0.149
Acetonitrile	139	0.05
Isopropanol	132	0.178
Pyridine	112.5	0.678
Nitrobenzene	108.3	0.261
Ethylene Dichloride	98.1	0.92
Methylene Chloride	97.6	1.62
Dioxane	94.6	0.85
Acetone	93.3	0.168
Chlorobenzene	90.2	2.91
Tetrahydrofuran	86.8	4.70
Chloroform	85.3	3.36
Benzene	83.6	3.42
Methyl Ethyl Ketone	81.7	0.55
Ethyl Acetate	81.6	0.50
Toluene	79.3	4.12
Mesitylene	77.4	3.06
Xylene	77.4	2.86
Carbon Tetrachloride	73.6	4.68
Cyclohexane	66.8	3.68
Ethyl Ether	59.8	1.52
n-Heptane	55.0	2.38
n-Hexane	52.4	2.32

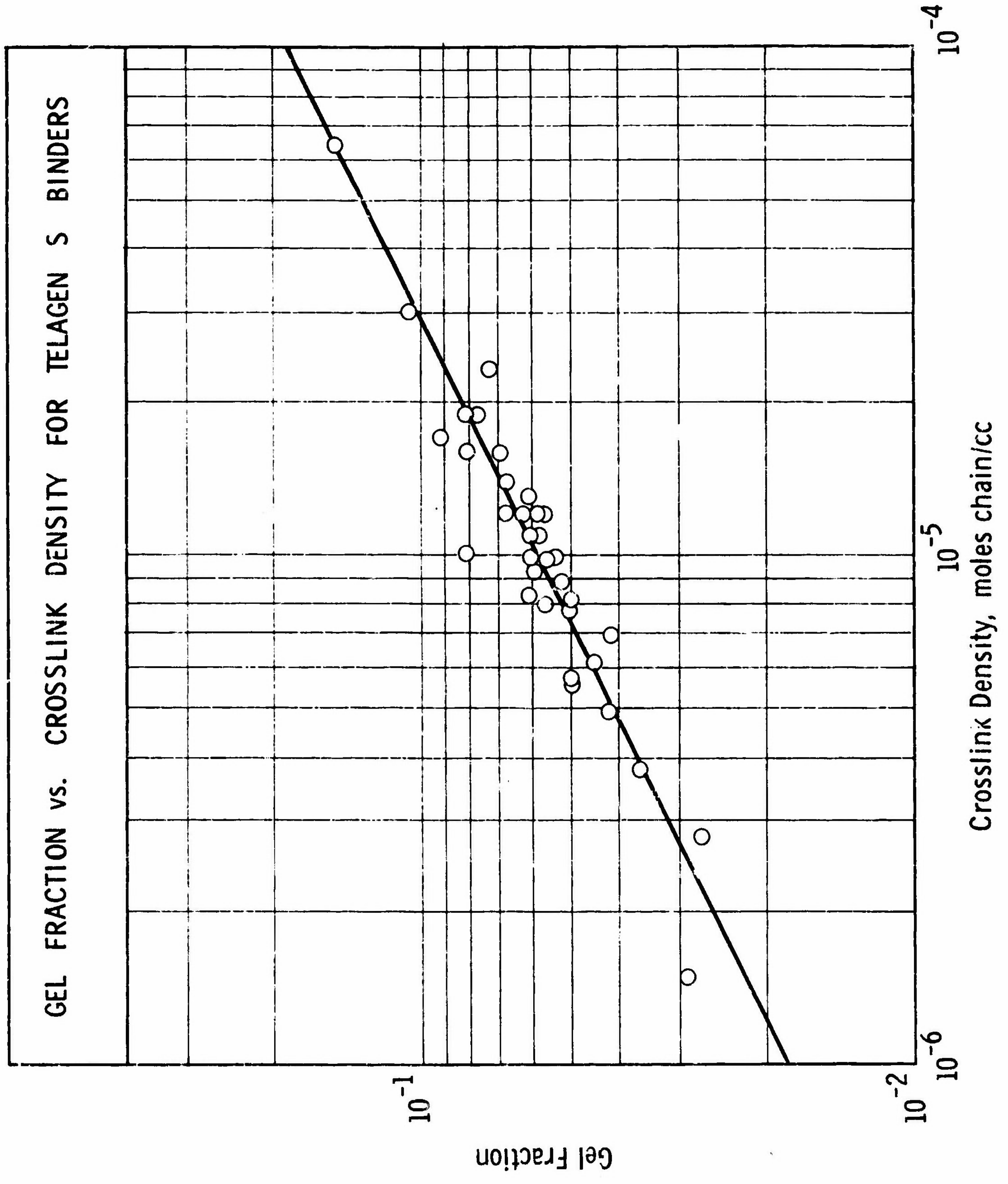

GEL FRACTION vs. CROSSLINK DENSITY FOR TELAGEN S BINDERS
10^{-4}
10^{-5}
10^{-6}
Crosslink Density, moles chain/cc
10^{-1}
10^{-2}
Gel Fraction

Figure 26

(U) Data obtained under Contract AF 04(611)-10386 indicated a linear correspondence of the C_1 constant for carboxy-terminated Telagen S cured with epoxides or with aziridines and the crosslink densities of these polymers. The C_1 constant for Telagen S-CTI-HDI elastomers showed no such correlation (see Figure 49 of Final Report, AFRPL-TR-66-40, Contract AF 04(611)-10386 (1)).

(U) Data accumulated under the present program show that the C_1 constants of plasticized Telagen S-CTI-HDI binders do correlate linearly with the crosslink densities (Figure 27). The line in Figure 27 is $\nu_e/V = 10^{-4}C_1$.

(U) The meaning of the C_2 with respect to the polymer properties is not known. Figure 28 indicates that C_2 is not a completely independent parameter, but depends to some extent upon C_1. The line represents the loci of points $C_1 = C_2$. The value of C_2 decreases with increasing plasticizer content (Figure 29), which would be expected if plasticization were like solvent swelling[5]. In none of the cases studied did $C_2 = 0$ so that ideal behavior would be expected.

i. Differential Thermal Behavior and Crosslink Densities of Telagen S Binders (U)

(U) The decomposition of isocyanate-cured Telagen S binders of various crosslink densities was studied by differential thermal analysis. A linear relationship of the crosslink density with the decomposition temperature was discovered (Figure 30).

j. Crosslink Density (U)

(U) The crosslink densities from compression moduli of toluene swollen binders and the crosslink densities from stress relaxation measurements at 150°F are compared in Figure 31. The stress relaxation data at 150°F gave lower crosslink densities than those at 77°F. The binders may not have reached complete equilibrium relaxation at 77°F and may not at 150°F either because crosslink densities from relaxation data were higher than those from compression moduli studies. Swelling of the binders for the compression moduli determination eliminated the effects of crystallinity and hydrogen bonding and minimized the effect of entanglements. For this reason, whenever possible, crosslink densities from compression of swollen binders have been used in this report for correlation work.

7. Propellant Studies (U)

a. Preparation, Castability, and Cure (U)

(U) Propellants were prepared to further test the effect of plasticizers, the effects of CTI to HDI ratio, NCO to OH ratio, plasticizers and catalyst levels, and replacement of DEA by C-1. All propellants contained 88 wt% solids. The propellants and their properties are shown in Tables XXIV-XXVI.

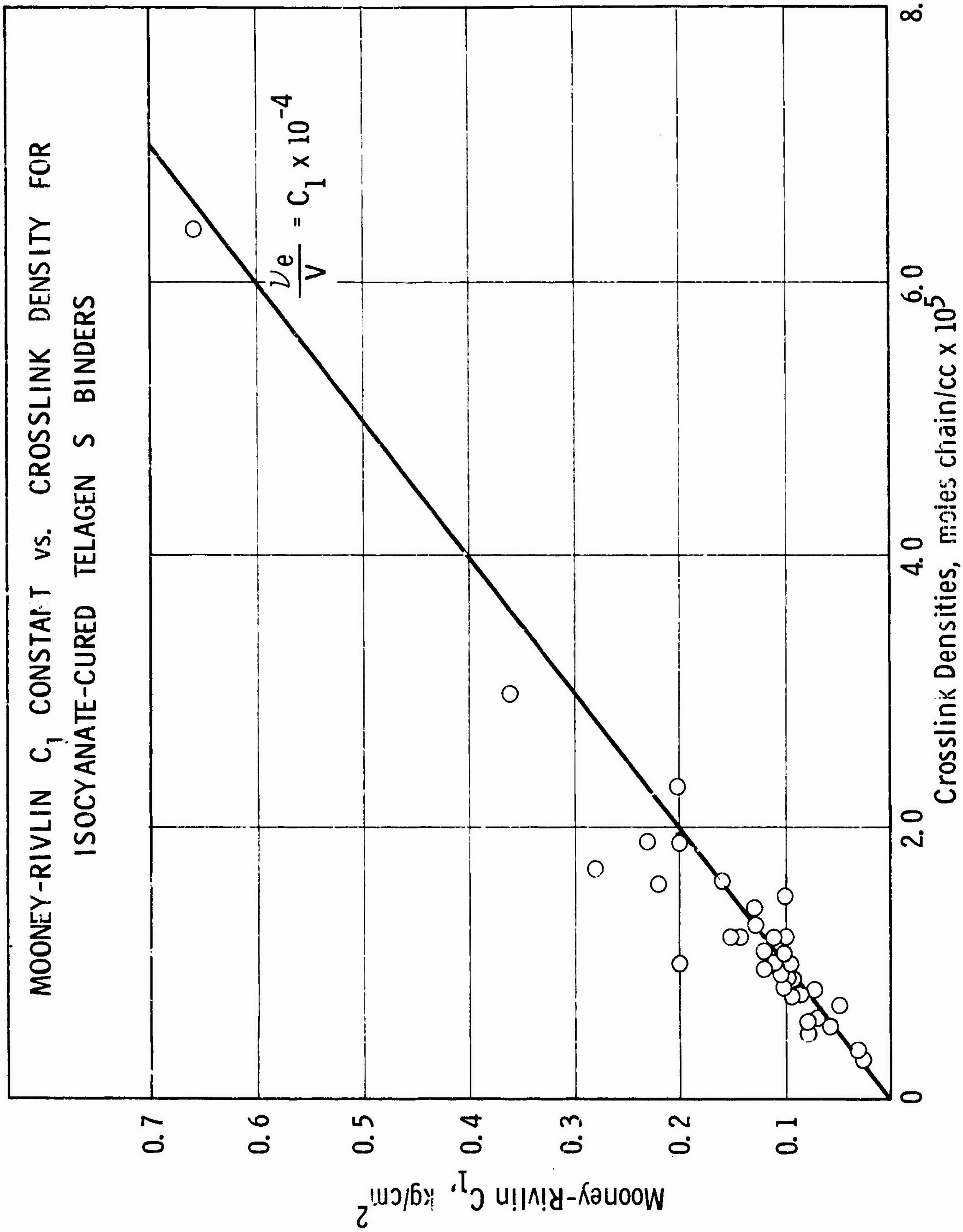

MOONEY-RIVLIN C_1 CONSTANT vs. CROSSLINK DENSITY FOR
ISOCYANATE-CURED TELAGEN S BINDERS
$\frac{\nu e}{V} = C_1 \times 10^{-4}$
0.7
0.6
0.5
0.4
0.3
0.2
0.1
Mooney-Rivlin C_1, kg/cm^2
0
2.0
4.0
6.0
8.0
Crosslink Densities, moles chain/cc x 10^5

Figure 27

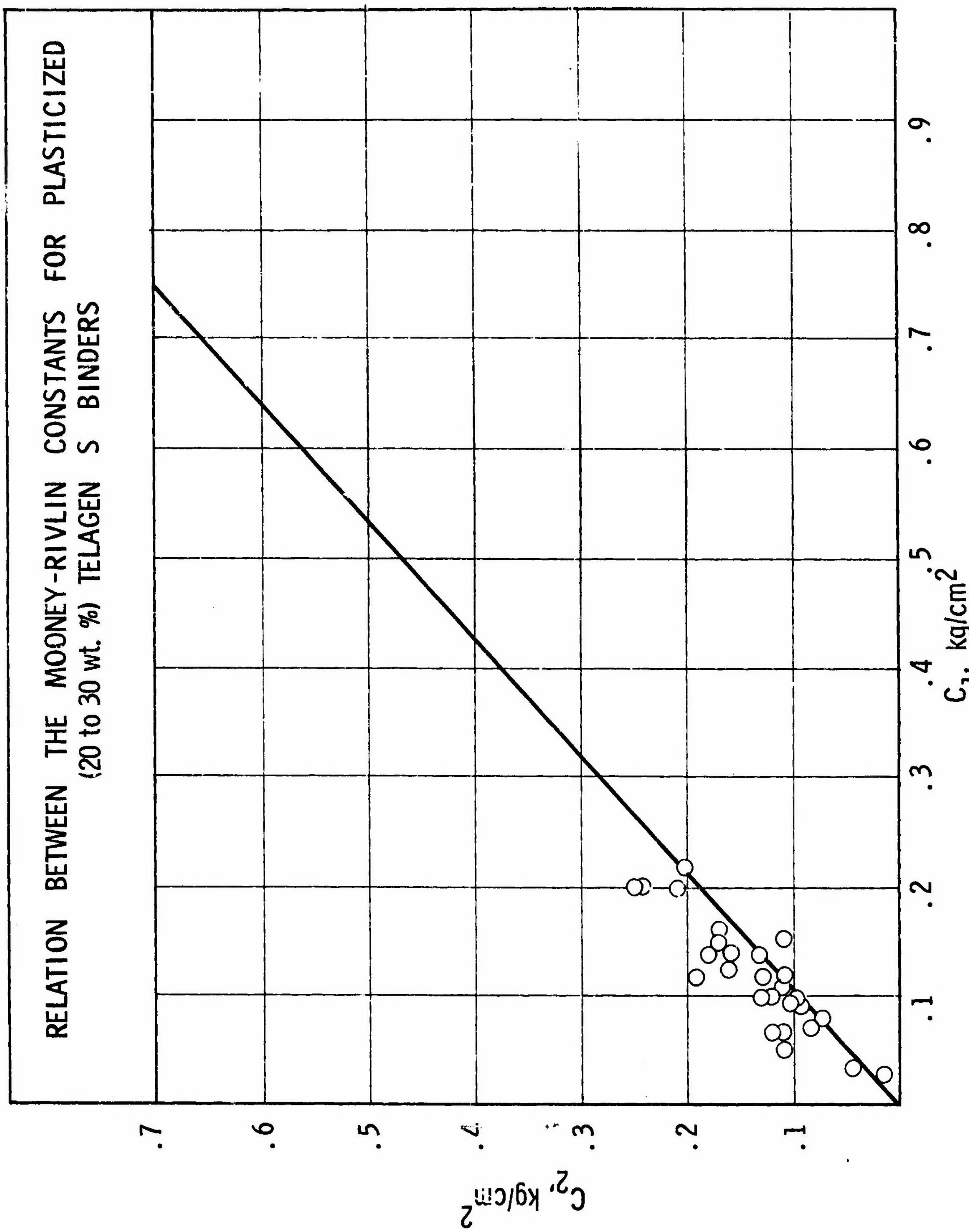

RELATION BETWEEN THE MOONEY-RIVLIN CONSTANTS FOR PLASTICIZED
(20 to 30 wt. %) TELAGEN S BINDERS
.1 .2 .3 .4 .5 .6 .7 .8 .9
C_1, kg/cm^2
.1 .2 .3 .4 .5 .6 .7
C_2, kg/cm^2

Figure 28

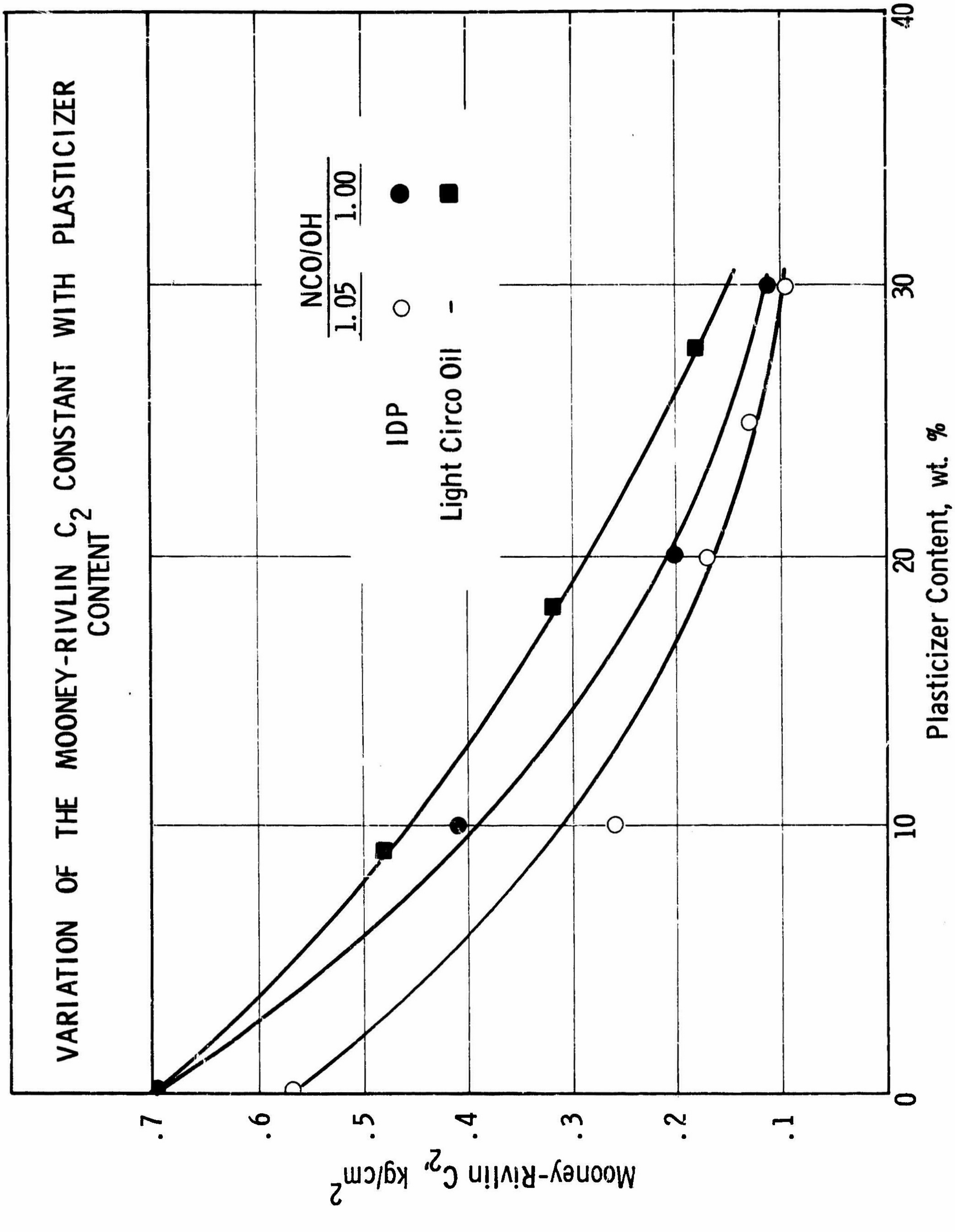

VARIATION OF THE MOONEY-RIVLIN C_2 CONSTANT WITH PLASTICIZER CONTENT[2]
NCO/OH
1.05
1.00
IDP
Light Circo Oil
-
Mooney-Rivlin C_2, kg/cm^2
.7
.6
.5
.4
.3
.2
.1
0
10
20
30
40
Plasticizer Content, wt. %

Figure 29

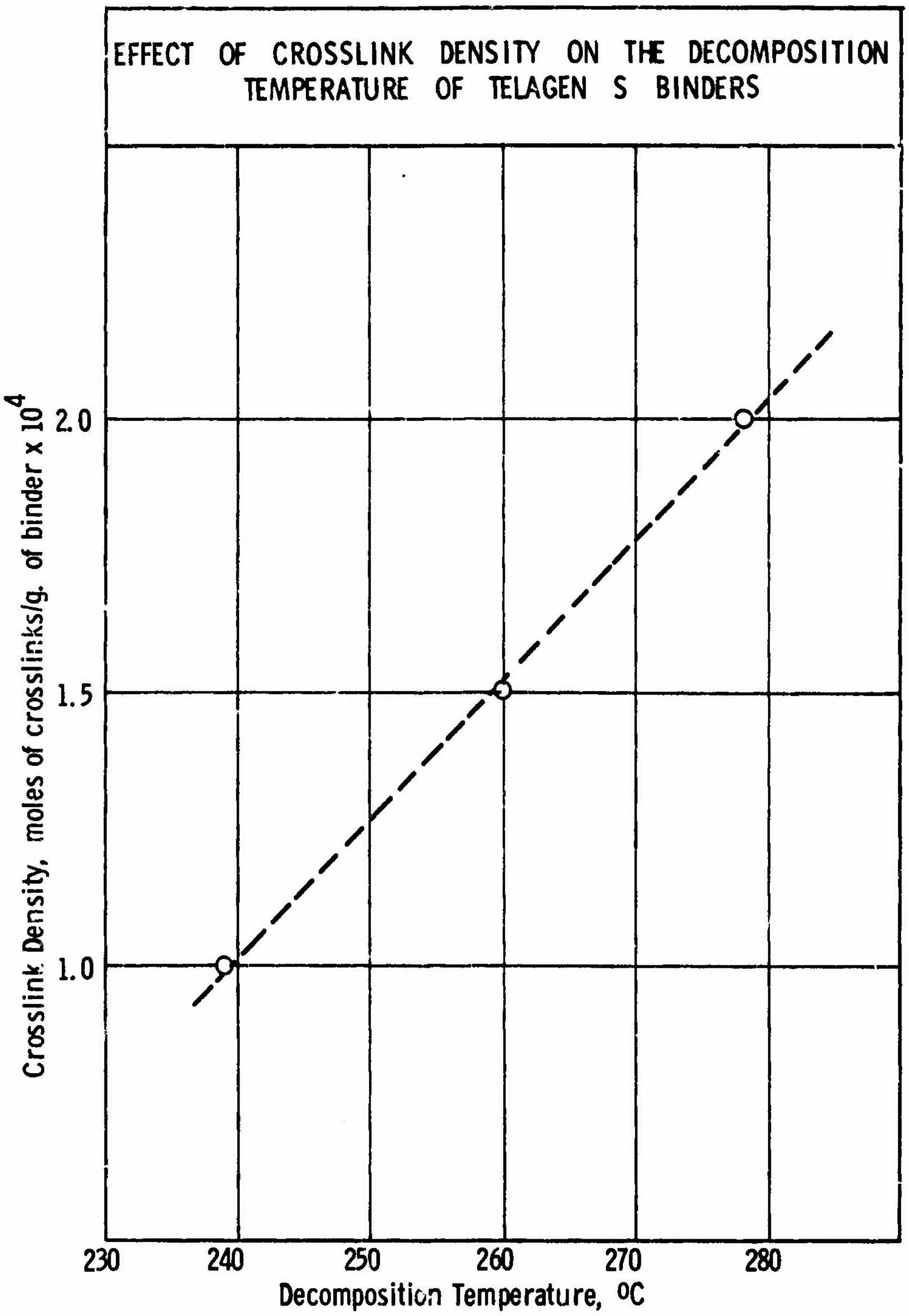
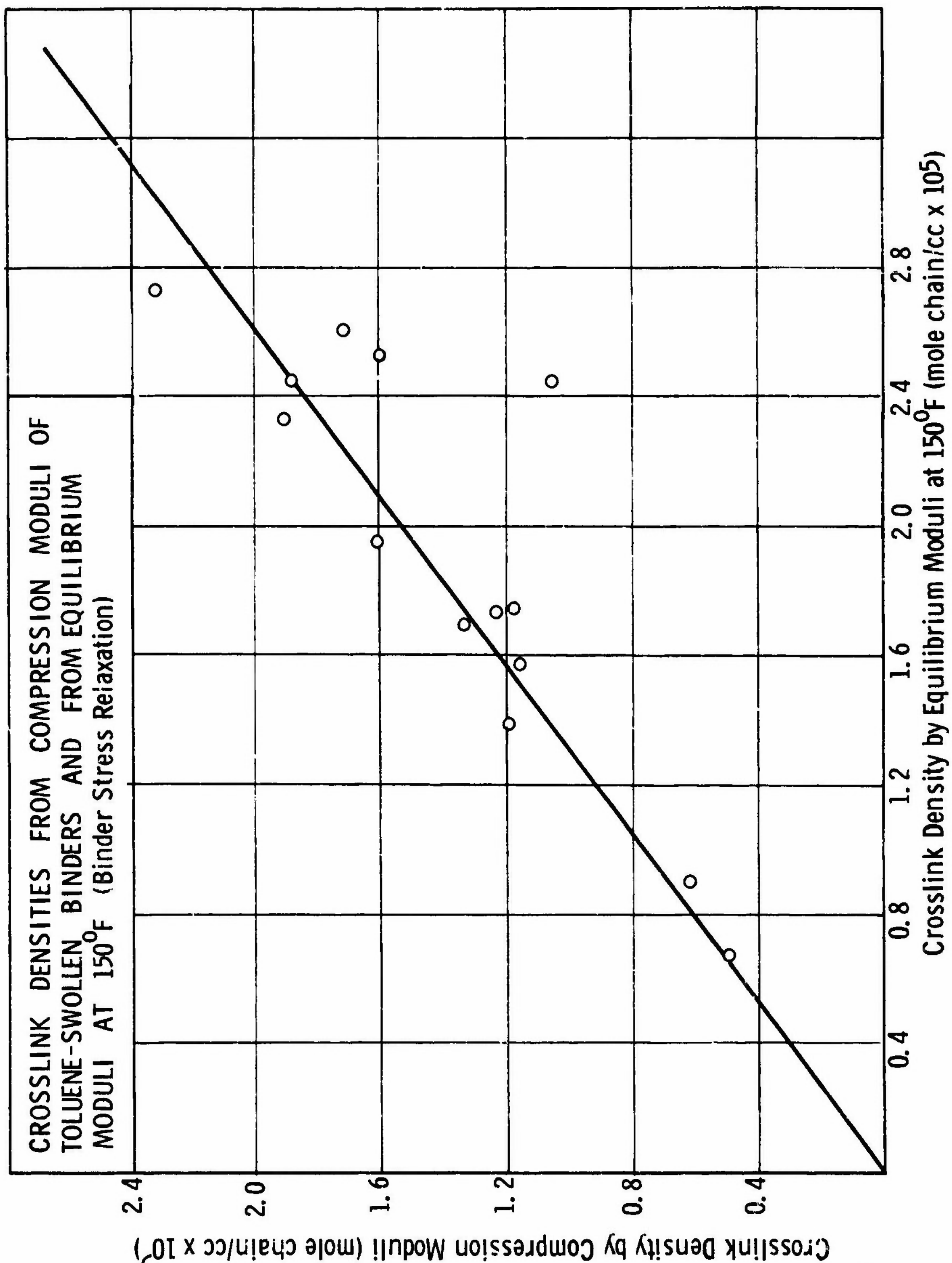

EFFECT OF CROSSLINK DENSITY ON THE DECOMPOSITION TEMPERATURE OF TELAGEN S BINDERS
Crosslink Density, moles of crosslinks/g. of binder x 10^4
2.0
1.5
1.0
230
240
250
260
270
280
Decomposition Temperature, °C

Figure 30



CROSSLINK DENSITIES FROM COMPRESSION MODULI OF TOLUENE-SWOLLEN BINDERS AND FROM EQUILIBRIUM MODULI AT 150°F (Binder Stress Relaxation)

Figure 31

Table XXIV

THE MECHANICAL BEHAVIOR OF TELAGEN S PROPELLANT

Reference No.	Plasticizer	Treatment[b]	NCO/OH	Castability at 135°F[c] Initial	1 hour	Cure Time, days at 135°F
1	Oronite 6	MS	1.05	20.5	19.5	12
2	DOZ	MS	1.05	21	22	12
3	S-141	MS	1.05	17	20	12
4	Light Circo Oil	none	1.05	20	17[f]	12
5	IDP	none	1.05	23	23	12
6	Oronite 6	MS	1.05	21	21	12
7	Nujol	MS	1.05	20	18[g]	7
8	IDP	none	1.00	23	22	7
9	IDP	SiO_2	1.00	-	-	8
10	IDP	SiO_2	1.05	-	-	8
11	IDP	SiO_2	1.10	-	-	8
12[h]	IDP	SiO_2	1.00	-	-	8

[a] All propellants were 50g batches and contained 75.6 vol % solids, Telagen S (8507-I-47.1) 90

[b] MS = dried over molecular sieves; SiO_2 = passed through column of SiO_2.

[c] Plastimeter reading (see final report Contract AF 04(611)-10386, p 166); > 22 = excellent, 20

[d] 15 sec.

[e] Bond failure.

[f] 2-1/2 hours.

[g] 1.5 hours.

[h] DEA replaced by C-1.

Table XXIV

VIOR OF TELAGEN S PROPELLANTS[a] (U)

...at 135°F[c] 1 hour	Cure Time, days at 135°F	Hardness,[d] Shore A Top	Side	Bottom	Mechanical Behavior at 77°F σ_{nm} psi	σ_{nb} psi	ϵ_{nm} %	ϵ_{nb} %	E_o psi
19.5	12	42	49	46	46	46	15	16	866[e]
22	12	43	67	72	129	129	18	18	1212[e]
20	12	14	48	48	58	58	23	25	354
17[f]	12	62	73	76	150	150	22	22	1740[e]
23	12	31	51	53	47	47	27	30	816
21	12	28	48	48	64	64	27	34	976
18[g]	7	43	70	72	110	110	20	20	1100
22	7	16	40	39	50	46	28	38	315
-	8	63	70	70	137	137	25	25	1160
-	8	53	65	73	141	141	28	28	1440
-	8	71	80	80	186	186	24	24	2120
-	8	30	35	35	61	54	32	43	420

Telagen S (8507-I-47.1) 90 eq., DEA 1.0 eq. and HDI:CTI = 4.0; plasticizer = 25 wt% of binder.

SiO_2.

(166); > 22 = excellent, 20-22 = good, 19-20 = fair, 16-19 = poor, and < 16 = not castable.

Table XXV

MECHANICAL BEHAVIOR OF TELAGEN S PROPELLANTS

Reference No.	Prepolymer Lot No.	Plasticizer	Treatment[b]	HDI/CTI	NCO/OH	Catalyst,%	Cure Time, days at 135°F
1	8507-I-47.1	IDP	SiO_2	3.5	1.05	FeAA 0.002 HAA 0.006	4
2	8507-I-47.1	DOS	None	3.5	1.05	FeAA 0.002 HAA 0.006	4
3	8507-I-47.1	IDP	SiO_2	3.5	1.00	FeAA 0.002 HAA 0.006	6
4	8507-I-47.1	IDP	SiO_2	4.0	1.05	FeAA 0.002 HAA 0.006	6
5	8507-I-47.1	Light Circo Oil	MS	3.5	1.05	FeAA 0.002 HAA 0.006	6
7	8507-I-47.1	DOS	None	3.5	1.05	FeAA 0.002 HAA 0.006	6
8	8507-I-47.1	DOS	None	3.5	1.05	FeAA 0.002 HAA 0.006	6
9	8507-I-47.1	DOS	None	3.5	1.05	CoAA 0.01	6
10	242AM-148AH	IDP	SiO_2	3.5	1.00	FeAA 0.002 HAA 0.006	6
11	242AM-148AH	DOS	None	3.5	1.00	FeAA 0.002 HAA 0.006	6
12	242AM-148AH	IDP	SiO_2	3.5	1.05	FeAA 0.002 HAA 0.006	6
13	242AM-148AH	DOS	None	3.5	1.05	FeAA 0.002 HAA 0.006	6
14	242AM-148AH	IDP	SiO_2	3.5	1.00	FeAA 0.0013 HAA 0.007	4
15	242AM-148AH	IDP	Red.	3.5	1.00	FeAA 0.002 HAA 0.006	4
16	242AM-148AH	Light Circo Oil	MS	3.5	1.00	FeAA 0.002 HAA 0.006	4
17	242AM-148A	IDP	SiO_2	3.5	1.00	FeAA 0.002 HAA 0.006	4
18	242AM-148AH	IDP	SiO_2	4.0	1.00	FeAA 0.002 HAA 0.006	6
19	242AM-148AH	IDP	None	4.0	1.00	FeAA 0.002 HAA 0.006	6
20	242AM-148AH	IDP	SiO_2	4.0	1.00	FeAA 0.002 HAA 0.006	6

Table XXV

F TELAGEN S PROPELLANTS[a] AT 77°F (U)

		Castability[c]		Hardness, 15 sec Shore A			Mechanical Properties				
yst,%	Cure Time, days at 135°F	Plastimeter Reading	Time, hrs	Top	Side	Bottom	σ_{nm} psi	σ_{nb} psi	ϵ_{nm} %	ϵ_{nb} %	E_o psi
0.002 0.006	4	18	1.5	74	80	71	174	165	31	33	800
0.002 0.006	4	21	0.5	80	66	65	168	164	33.5	37	775
0.002 0.006	6	20	0.0	68	63	72	197	192	29.5	31	990
0.002 0.006	6	21.5	0.0	73	73	75	141	133	36	40	600
0.002 0.006	6	20	0.0	82	86	82	225	215	31.5	35	1200
0.002 0.006	6	22	0.0	78	69	73	169	164	30	32.5	885
0.002 0.006	6	22	0.5	78	70	79	163	161	30	32	815
0.01	6	13.5	0.5	69	76	81	121	119	32	33.5	810
0.002 0.006	6	22	0.25	64	66	66	185	180	28	29	1065
0.002 0.006	6	18	0.75	66	67	69	192	186	27.5	28.5	1105
0.002 0.006	6	22.5	0.0	74	70	77	178	174	25.5	26.5	1015
0.002 0.006	6	23	0.0	68	67	71	176	172	26	27	1036
0.0013 0.007	4	23.5	0.25	66	67	66	155	144	27	28	890
0.002 0.006	4	23	0.25	64	64	71	178	-	27	28	1015
0.002 0.006	4	19.5	0.25	73	74	79	208	200	26	29	1275
0.002 0.006	4	21.5	1	72	68	72	165	-	22	23	1150
0.002 0.006	6	23.5	0	50	49	49	113	104	33	35	480
0.002 0.006	6	23	0.5	50	53	52	105	99	36	40	430
0.002 0.006	6	24	0.25	58	47	57	128	122	31	33	585

2

Table XXV (Continued)

Reference No.	Prepolymer Lot No.	Plasticizer	Treatment[b]	HDI/ CTI	NCO/ OH	Catalyst,%	Cure Time, days at 135°F	Ca Plast Read
21	242AM-148AH	Squalene	Red.	4.0	1.00	FeAA 0.002 HAA 0.006	6	20
23	242AM-148AH	DOS	SiO_2	4.0	1.00	FeAA 0.002 HAA 0.006	5	23
24	242AM-148AH	IDP	SiO_2	4.0	1.05	FeAA 0.002 HAA 0.006	6	22
25	242AM-148AH	IDP	SiO_2	3.5	1.00	FeAA 0.002 HAA 0.006	5	17
26	242AM-148AH	IDP	SiO_2	4.0	1.00	FeAA 0.002 HAA 0.006	6	-
27	242AM-148AH	$C_{11}H_{23}CN$	None	4.0	1.00	FeAA 0.002 HAA 0.006	6	-
28	242AM-148AH	IDP	SiO_2	4.0	1.00	Niax D-22 0.004 HAA 0.006	6	-
9254	242AM-158H	IDP	SiO_2	4.0	1.00	FeAA 0.002 HAA 0.006	7	-
9255	242AM-158H	IDP	SiO_2	3.5	1.00	FeAA 0.002 HAA 0.006	7	-
9256	242AM-158H	IDP	SiO_2	4.0	1.00	FeAA 0.004 HAA 0.008	7	-

[a] All propellants were 400-gm batches cured at 135°F and contained 73% NH_4ClO_4 (LC blend), 15% Al(
(25 wt% of binder)(Conf.). All contained 0.1% C-1 except #20 and #24 (0.2%) and #25 and #26 whi

[b] SiO_2 = passed through column of silica gel; MS = dried over molecular sieve; Red. = redistilled.

[c] 60 sec. plastimeter reading taken at the indicated hours after casting; > 22 = excellent, 20-22

V (Continued)

	Cure Time, days at 135°F	Castability[c] Plastimeter Reading	Castability[c] Time, hrs	Hardness, 15 sec Shore A Top	Hardness, 15 sec Shore A Side	Hardness, 15 sec Shore A Bottom	Mechanical Properties σ_{nm} psi	σ_{nb} psi	ϵ_{nm} %	ϵ_{nb} %	E_o psi
	6	20	0.75	20	27	30	60	53	47	57	185
	5	23.5	0.25	62	60	60	160	153	32	36	760
	6	22	0.25	66	60	64	147	140	30	32	700
	5	17	0.25	53	49	54	94	88	22	25	580
	6	-	-	-	-	-	65	61	26	30	450
	6	-	-	83	68	68	142	135	26	29	880
0.004	6	-	-	38	36	38	63	61	24	27	320
	7	-	-	51	-	-	90	88	42	50	304
	7	-	-	59	-	-	112	110	38	41	420
	7	-	-	55	-	-	84	81	44	52	313

ClO_4 (LC blend), 15% Al(H15), Telagen S, HDI and CTI and plasticizer
0.2%) and #25 and #26 which contained no C-1, and all were processed at 110-120°F.

eve; Red. = redistilled.

> 22 = excellent, 20-22 = good, 19-20 = fair, 16-19 = poor, and < 16 = not castable.

Table XXVI

MECHANICAL BEHAVIOR OF TELAGEN S PROPELL

Prepolymer Lot No.	Reference No. 10-GP-	Plasticizer	Treatment[b]	HDI/CTI	NCO/OH	Catalys
242AM-148AH	7344	IDP	SiO_2	4.0	1.00	FeAA 0. HAA 0.
242AM-148AH	7345	IDP	SiO_2	4.0	1.05	FeAA 0. HAA 0.
242AM-148AH	7516	DOS	SiO_2	4.0	1.00	FeAA 0. HAA 0.
242AM-148AH	7517	IDP	SiO_2	4.0	1.00	FeAA 0. HAA 0.
242AM-148AH	7707	IDP	SiO_2	4.0	1.00	FeAA 0. HAA 0.
242AM-148AH	7825	Light Circo Oil	MS	4.25	1.00	FeAA 0. HAA 0.
242AM-148AH	7826	DOS	None	4.0	1.00	FeAA 0. HAA 0.
242AM-148AH	9569	IDP	SiO_2	4.0	1.02	FeAA 0. HAA 0.
242AM-158H	9570	IDP	SiO_2	3.5	1.02	FeAA 0. HAA 0.
242AM-148AH	9614	DOS	None	4.0	1.02	FeAA 0. HAA 0.
242AM-158H	9615	IDP	SiO_2	3.5	1.00	FeAA 0.0 HAA 0.0

[a] All propellants were 3200-gm batches and contained 73% NH_4ClO_4 (LC blend), 15% Al(H15), Tel and plasticizer (25 wt% of binder) (Conf). All were processed at 120-125°F.

[b] SiO_2 = passed through silica gel; MS = dried over molecular sieve.

Table XXVI

OF TELAGEN S PROPELLANTS[a] AT 77°F (U)

NCO/OH	Catalyst,%	Cure Time, days at 135°F	Hardness, Shore A, 15 sec. Top	Side	Mechanical Properties σ_{mm} psi	σ_{mb} psi	ϵ_{mm} %	ϵ_{mb} %	E_0 psi
1.00	FeAA 0.002 HAA 0.0063	6	58	59	108	106	35	36	460
1.05	FeAA 0.002 HAA 0.0063	6	65	61	145	141	32	34	675
1.00	FeAA 0.0023 HAA 0.0063	7	60	66	130	125	36	40	550
1.00	FeAA 0.0023 HAA 0.0063	11	63	71	76	74	31	34	1000
1.00	FeAA 0.0031 HAA 0.0094	8	68	65	121	116	34	38	525
1.00	FeAA 0.0023 HAA 0.0063	4	73	66	170	165	34	37	830
1.00	FeAA 0.0023 HAA 0.0063	4	68	62	121	118	28	30	570
1.02	FeAA 0.002 HAA 0.006	7	-	-	119	118	32	34	546
1.02	FeAA 0.002 HAA 0.006	7	-	-	81	77	44	53	291
1.02	FeAA 0.002 HAA 0.006	7	-	-	114	113	33	35	514
1.00	FeAA 0.002 HAA 0.006	7	-	-	64	59	51	64	231

lend), 15% Al(H15), Telagen S, HDI, CTI, C-1 (0.1%, except 0.2% for 7517 and 7707)
0-125°F.

2

(U) The propellant bars (3/8" x 2/8" x 2.7") were tested for uniaxial tensile behavior at 77°F. Only gross effects were observed by this procedure. The propellants made in 50-g. batches were noticeably softer on the surface exposed to air. This phenomenon was also observed during work under Contract AF 04(611)-10386; but the surface softness was not detected with larger batches (> 1-lb).

(U) The castability at 135°F was determined by the Parallel Plate Plastimeter. This consisted of two heavy glass plates on one of which was placed a cylindrical sample of propellant. The other glass plate was lowered on to the sample. The spread of the propellant was noted after 30 seconds. The change in castability with time was an indicator of the rate at which the propellant was curing. The propellants with the exception of No. 3, Table XXIV, plasticized with S-141 had good to excellent initial castability even one hour after casting. No difficulty was experienced with castability or cure of these propellants even at the 125-lb scale.

b. Propellant Cure Rate (U)

(U) The cure rate and castabilities of some of these propellants are indicated by the plastimeter readings summarized in Table XXVII. Propellants with IDP or DOS had suitable cure rates whereas the cure rate of those with Light Circo Oil was too fast (marginal potlife). By adjusting the amount of curing agent in the propellant, the system could be optimized and the overall properties improved. Diethanolamine was a catalyst for this system and increased the crosslink density of the propellant binder.

Table XXVII

CASTABILITY AND CURE RATE OF TELAGEN S PROPELLANTS[a] AT 135°F (U)

Reference No. 10GP-	Plasticizer	Catalyst, Wt %	Plastimeter Reading[b] Time after Casting, hr .25	1.0	1.25	1.5	2.5	3.5	3.75	5.75
7707	IDP	FeAA.0031 HAA .0094	24.5	-	-	-	19.5	-	-	-
7708	IDP	FeAA.0023 HAA .0063	-	21.5	-	-	-	14.5	-	-
7709	IDP	FeAA.0023 HAA .0063	23.5	-	-	-	-	-	19.5	18.0
7825	Light Circo Oil	FeAA.0023 HAA .0063	-	-	-	17.0	-	-	-	-
7826	DOS	FeAA.0023 HAA .0063	-	-	23.5	-	-	-	-	-

[a]Compositions shown in Table XXVI. No. 7708 contains 0.05 DEA and 7709, 0.1% C-1; otherwise they were similar to 7707. Propellants 7708 and 7709 were not tested further.

[b]Castability - plastimeter reading relation: > 22, excellent; 20-22, good; 19-20, fair; 16-19, poor; < 16, not castable.

(U) The cure rate was relatively fast with propellants processed at 125°F, but was slowed by processing at 110°F. A propellant similar to No. 10 (Table XXV) but containing 0.0013% FeAA and 0.007% HAA, was divided and samples were cured at 110°F and 135°F. Plastimeter readings for the samples taken over a period of seven hours are shown in Table XXVIII.

Table XXVIII

PLASTIMETER READINGS OF PROPELLANT CURING AT 110°F and 135°F (U)

	Time after Casting, hours				
Temperature	0.25	1	3.25	4.5	6.75
110°F	23	23.5	20	18.5	16.5
135°F		21.5	15		

While there was considerably more potlife at the lower temperature, both propellants cured normally.

(U) Niax D-22, the catalyst in Propellant 28 (Table XXV), gave a rapid cure rate, the propellant beginning to cure in the mixer. Previously when CoAA was used as a catalyst, the propellant had a suitable cure rate but did not give a complete cure in formulations which contained C-1 as the bonding agent. When DEA was used as the bonding agent, CoAA gave a more complete cure.

(U) As a result of these studies, the catalyst recommended for the workhorse propellant is FeAA 0.002% plus HAA 0.006% with IDP and C-1 in the formulation. This would allow processing at 120°F with adequate potlife.

c. Effect of Plasticizers (U)

(U) The observations made concerning the effects of plasticizers on the behavior of Telagen S binders were also true for propellants. The effects were, however, less pronounced for propellants. The following observations substantiate the plasticizer effect in propellants.

(U) Comparison of propellants made with nontreated and treated IDP indicates the effect of plasticizer-curing agent interaction. With IDP which had been passed through a column of SiO_2, propellants with better properties (compare 5 with 10 and 8 with 9 in Table XXIV) resulted. With the nontreated IDP, a lower modulus than that of propellant with SiO_2 treated plasticizer (see No. 18, 19 and 20, Table XXV) was always obtained. The IDP passed through silica gel was therefore used exclusively for this study.

(U) Propellants plasticized with Light Circo Oil had higher moduli and higher tensile strengths than propellants plasticized with either

DOS or IDP. The same results were obtained in the binder studies. Possibly the cure reaction was more complete when Light Circo Oil was used as a plasticizer. Compare Propellants 4 and 5, Table XXIV and Propellants 1, 2, and 5, Table XXV.

(U) Propellants plasticized with squalene (Propellant 21, Table XXV) showed poor mechanical behavior. This confirmed the work done earlier on binders and indicated that squalene interfered with the cure. Propellant 27 (Table XXV) plasticized with n-undecyl cyanide was relatively hard. The surface was harder than expected, probably because some plasticizer was lost by evaporation during cure.

(U) Figure 32 summarizes the effect of plasticizer cure interference on the initial uniaxial moduli of Telagen S propellants. The data were scattered and the demonstration of an effect not as conclusive as with binders. However, the effect does exist and considerable data have been cited to show it. It is also very likely that in propellants, other plasticizer factors, such as compatibility, exert strong influences on properties.

d. Bonding Agents (U)

(U) During the propellant optimization studies made under Contract AF 04(611)-10386, it became apparent that binder reinforcement around the oxidizer was required. Diethanolamine was added to the propellant for this purpose. The theory was that the basic diethanolamine would be attracted to the acidic oxidizer surface where it would react to form diethanolammonium perchlorate and ammonia. The amine salt could then react with isocyanate as a diol to reinforce the binder around the oxidizer. This theory assumed that the hydrogens on the nitrogen of protonated diethanolamine would not be available for reaction with the isocyanate.

(U) In Propellant 12 in Table XXIV, the diethanolamine was replaced by C-1, (N,N-di-(β-cyanoethyl)-2,3-dihydroxypropylamine) which had been used at Aerojet for some time to reinforce the oxidizer-binder interface[7]. The much lower initial modulus of Propellant 12 indicates that diethanolamine was responsible for crosslinking in the propellant. Further studies were made with C-1 to better evaluate it and to compare its effects with those of the diethanolamine.

(U) In Propellants 20 and 24, the amount of C-1 was increased and Propellants 25 and 26 were prepared without C-1. With increased amounts of C-1, a slightly harder propellant resulted, whereas propellants without C-1 showed poorer mechanical properties.

(U) Except for Propellant 21, the ϵ_m and the ϵ_b values were nearly the same, hence, oxidizer dewetting was minimal.

(U) The results of this work led to the use of 0.1% C-1 in propellant formulations. DEA is an important alternative bonding agent which because of its higher (than C-1) thermal stability will be useful in high temperature propellants.

PLASTICIZER CURE INTERFERENCE AND INITIAL MODULUS OF TELAGEN S PROPELLANTS

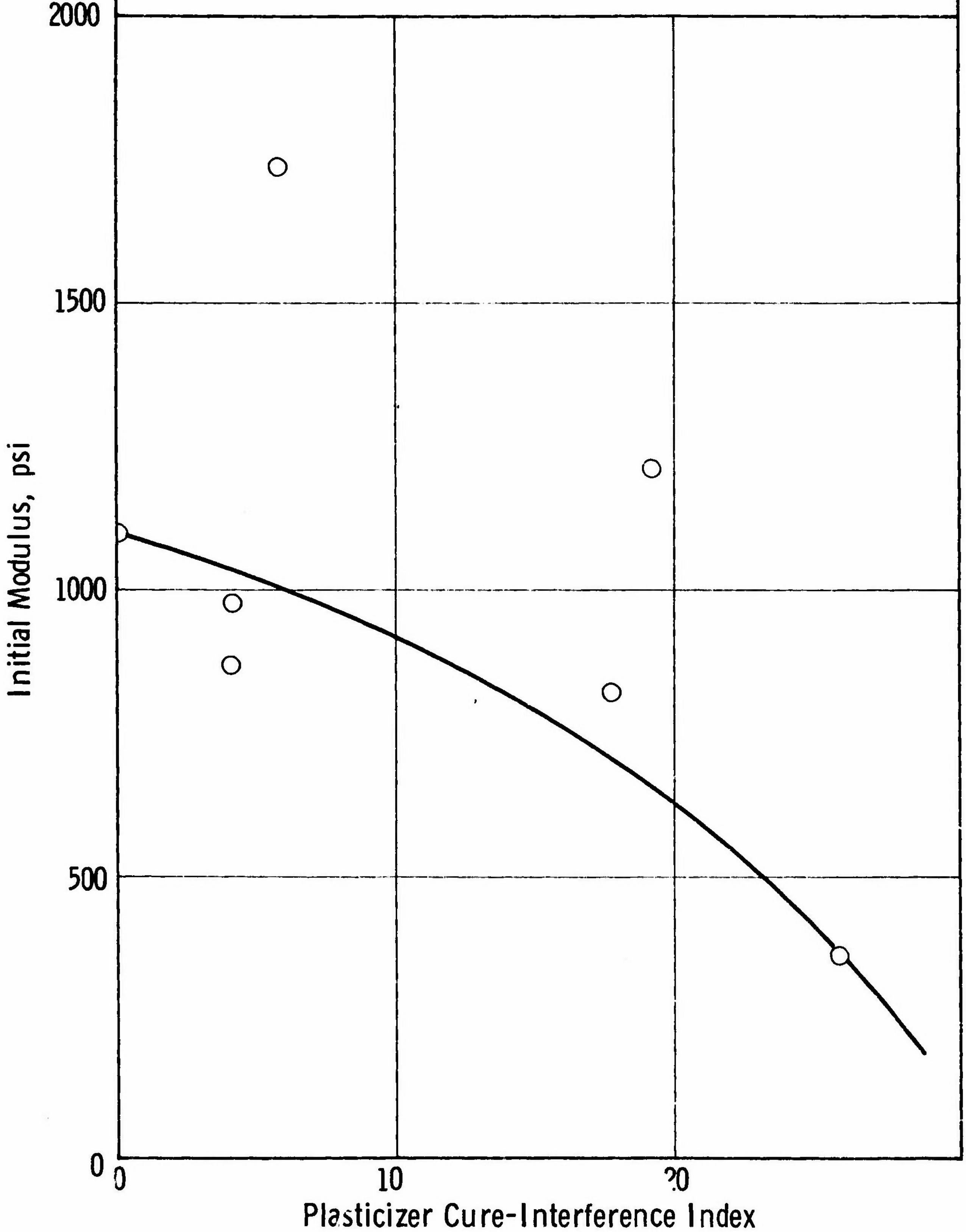


Figure 32

e. Cure Stoichiometry (U)

(U) The cure stoichiometry of the Telagen S propellants were more difficult to establish than that of the binders. It may be recalled that the best cures with binders were obtained at an NCO to OH ratio of 1.00.

(U) The initial studies (50-gram scale) indicated that, for the propellants containing SiO_2 treated IDP, an NCO to OH ratio of 1.05 is best (compare Propellants 9, 10 and 11, Table XXIV). The data for propellants made at the 400-gram scale were more ambiguous, although there was evidence that an NCO to OH ratio of 1.05 was better than one of 1.00. Thus, comparison of Propellants 2, 7, and 8 (Table XXV) with 11 favored a ratio of 1.00, but Propellant 11 uses a different prepolymer lot. A more valid comparison, Propellants 1 and 3 (Table XXV) favored a ratio of 1.00 for stoichiometric cure which is supported by comparison of Propellant 10 with 12. An NCO to OH ratio of 1.05 was indicated to be more stoichiometric by Propellants 20 and 24 which however contained greater amounts of C-1 than did the other propellants in Table XXV.

(U) These data pointed to a stoichiometric NCO to OH ratio between 1.00 and 1.05. Ten-pound batches were made at a ratio of 1.02. Propellants 7344, 7345, and 9569 have properties which favored the ratio 1.02, and the properties of Propellants 9570 and 9615 also supported the conclusion that the stoichiometric NCO to OH ratio was 1.02 for Telagen S propellants. Based upon these results, the large propellant batches were made with an NCO to OH ratio of 1.02.

(U) The propellant properties were adequately controlled by varying the HDI to CTI ratio. The change of this ratio from 4.0 to 3.5 gave much higher moduli (see Tables XXV and XXVI). This allowed a method of controlling the mechanical behavior of propellants made with a prepolymer of lower functionality. This was illustrated by Propellants 9254 and 9255 (Table XXV) made with Prepolymer 242AM-158H which was lower in functionality. Here the use of an HDI to CTI ratio of 3.5 gave adequate mechanical properties.

f. Low Temperature Properties (U)

(U) As was indicated by the binder studies, low temperature properties of propellants were not improved. Some low temperature, mechanical data are shown in Table XXIX.

g. Propellant Burning Rates (U)

(U) A preliminary strand burning rate study was made for an NH_4ClO_4-Al propellant (88 wt% solids) similar to No. 4 in Table XXV. The burning rates at 400 and 700 psia were 0.20 and 0.27 in./sec, respectively, at 80°F. Over the range 400 to 1500 psia, the pressure exponent of burning was 0.70. The pressure exponent was high compared to unsaturated hydrocarbon binders with the same solids, and would require further study to lower it. The burning rate studies are summarized in Figure 33. Further studies made with a propellant of higher solids loading substantiated the high burning rate-pressure exponent.

Table XXIX

MECHANICAL BEHAVIOR OF TELAGEN S PROPELLANTS[a] AT -75°F (U)

Reference No.	Mechanical Properties, 77°F/-75°F σ_m psi	σ_b psi	ϵ_m %	ϵ_b %	E_o psi
7344	108/1070	106/1065	35/4	36/4	460/47500
7345	145/1050	141/1045	32/3	34/4	675/46500
7707	121/1205	118/1200	34/4	38/4	525/52400

[a] Propellant composition in Table XXVI.

h. Large Propellant Batches (U)

(U) Two 125-lb batches of propellant were prepared for the aging studies under Phase Four of this program. The composition of these are shown in Table XXX.

Table XXX

COMPOSITION OF TELAGEN S PROPELLANTS PREPARED IN 125-LB BATCHES (U)

(C)

Component	Batch Composition, Wt% 1	2
NH_4ClO_4 35% + 48 35% SS 30% MA	73.00	73.00
Al H15	15.00	15.00
Telagen S	8.19[a]	8.21[b]
C-1	0.10	0.10
IDP[c]	3.00	3.00
HDI	0.58	0.56
CTI	0.13	0.14
HAA	0.006	0.006
FeAA	0.002	0.002

[a] Lot 242AM-148AH
[b] Lot 242AM-158H
[c] Passed through column of SiO_2.

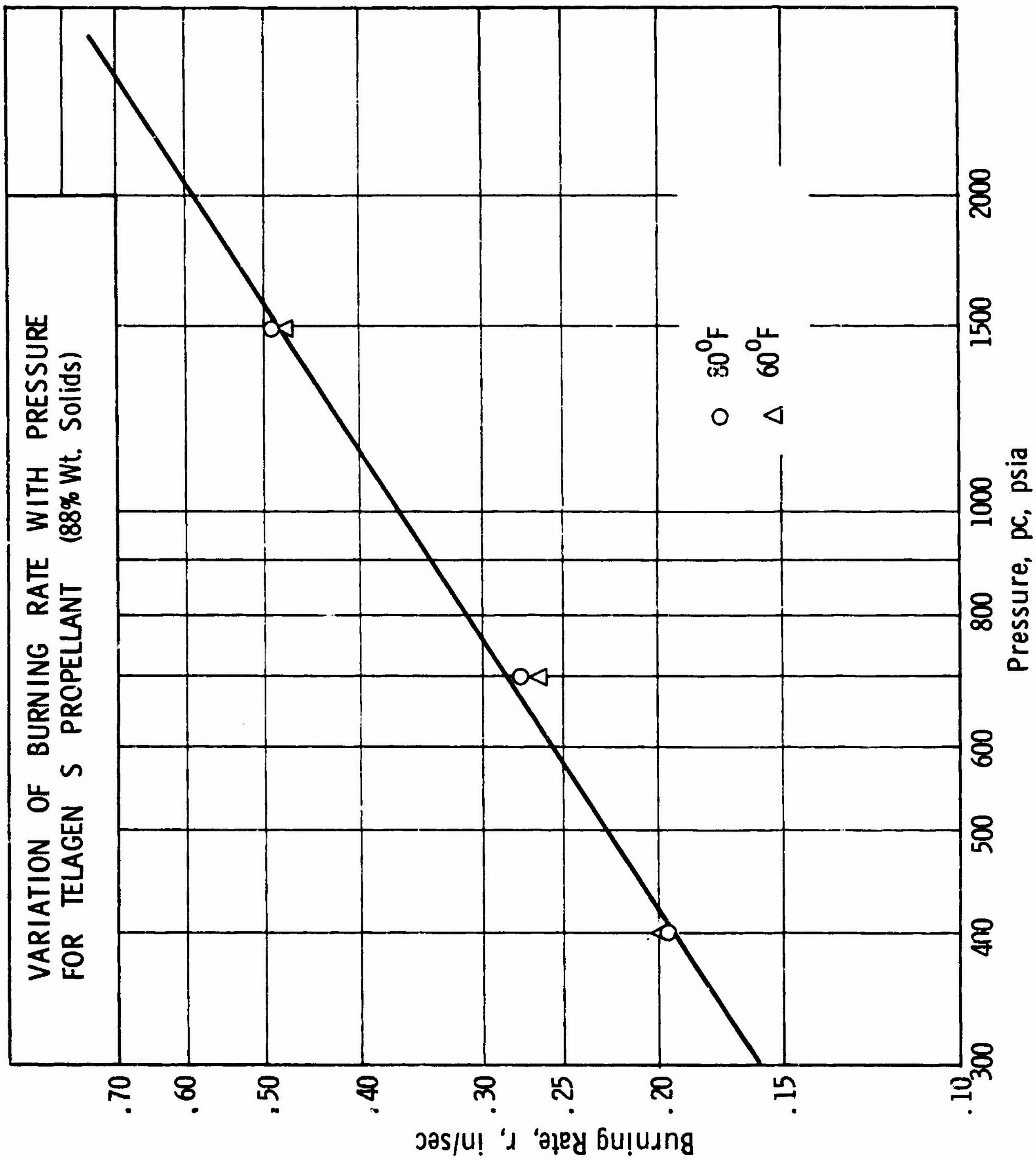

VARIATION OF BURNING RATE WITH PRESSURE
FOR TELAGEN S PROPELLANT (88% Wt. Solids)
○ 30°F
△ 60°F
Burning Rate, r, in/sec
.70
.60
.50
.40
.30
.25
.20
.15
.10
Pressure, pc, psia
300
400
500
600
800
1000
1500
2000

Figure 33

(U) Both propellants were mixed without any difficulty. The plastimeter reading was 24.5 for the first and 22 for the second 1¼ hours after casting which indicates excellent castability. The potlife was more than sufficient for this size batch. After curing 10 days, the Shore A hardness of the first was 63 (15 sec) on the top and 59 on the side. The propellant was cut into blocks for the aging studies.

(U) Some bars were pressed into test samples and the properties of the first propellant are listed in Table XXXI.

Table XXXI

MECHANICAL PROPERTIES OF PROPELLANT[a] PREPARED FROM TELAGEN S PREPOLYMER (U)

Test Temp. °F	σ_{nm} psi	σ_{nb} psi	ϵ_m %	ϵ_b %	E_0 psi
180	39	37	18.5	24	330
77	100	93	23.5	28	650
-75	1140	1100	3	3	58,500

[a]Propellant 1, Table XXX

(U) The second of these propellants has not been tested yet.

i. Cycling Motor (U)

(U) The analogue motor, containing Propellant No. 1, Table XXX, cycled to failure by changing the temperature at 24 hour intervals. The data are shown in Table XXXII.

Table XXXII

CYCLING OF THE ANALOGUE MOTOR[a] CONTAINING TELAGEN S PROPELLANT[b] (U)

Temp., °F	Strain, %
135	-
77	4.5
40	7.7
0	11.5
-40	14.8
-65	failed

[a]Chamber capped and desiccated; core size - 1.2 in.
[b]Propellant 1, Table XXX.

(U) These data indicate that the low temperature motor behavior of Telagen S propellants is not as poor as the low temperature mechanical behavior would suggest. Comparison with the current Minuteman Wing VI, Second-Stage propellant shows the Telagen S propellant to be at least as good and perhaps better. The controlling factor is the initial modulus at 77°F of the propellant.

(U) In any case the propellant was able to go to -40°F at a motor strain of about 15% without failure.

8. Maximum Solids Loaded Propellant (U)

a. Solids Loading and Packing (U)

1) Ratio of Solids to Binder Volumes (U)

(U) One of the advantages of a propellant binder with a highly efficient network structure is its ability to retain good mechanical properties when loaded with a greater amount of ballistic solids. Notwithstanding this advantage, the problem of achieving a higher solids loading without loss of mechanical properties is a difficult one. This is demonstrated by the ratio of the solids volume to the binder volume (including the plasticizer) and the volume fraction of solids for a number of actual and projected systems with a saturated hydrocarbon binder (Table XXXIII).

Table XXXIII

THE RATIO OF SOLIDS TO BINDER VOLUMES AND VOLUME FRACTION OF SOLIDS FOR VARIOUS PROPELLANT SYSTEMS (U)

Propellant	Wt % Solids	Volume Fraction of Solids	Solids to Binder Volume Ratio
Polaris	75	62.4	1.6
Minuteman Wing II (2nd Stage)	82.2	69.0	2.2
Tartar (sustainer)	82	70.0	2.3
Minuteman Wing VI (2nd Stage)	88	76.6	3.3
System 1[a]	90	80.2	4.1
System 2[a]	92	84.0	5.2

[a]System 1: 80% NH_4ClO_4, 10% Al; System 2: 84% NH_4ClO_4, 8% Al.

(U) As the solids loading increases beyond the state-of-art value of 88 wt%, the solids to binder volume ratio increases greatly. This ratio becomes even greater at low temperature since the volume of the binder decreases more rapidly than that of the filler.

2) <u>Importance of Particle Packing</u> (U)

(U) The importance of packing of solid particles is well known as exemplified by the extensive use of bi- and trimodal particle blends in solid propellants to obtain improved mechanical behavior. The ballistic requirements will normally establish an average particle size for the fillers of a solid propellant but there are limitless numbers of particle size distributions which will have the same average particle size. As a result the task of determining which blend of particle size distributions will achieve the highest solids loading in a propellant with reasonable mechanical properties is a tedious one.

b. Effect of Packing on Viscosity of Filled Liquids (U)

(U) A convenient method for determining the effectiveness of particle packing is by measuring the effect of particle packing on the viscosity of a liquid. The Eilers equation[8] shown below relates the relative viscosity (η_r) of a suspension to particle packing and loading.

$$\eta_r = \frac{\eta}{\eta_o} \quad 1 + \left[\frac{1.25\,\phi}{1-(\phi/\phi_f)} \right]$$

where η and η_o are the viscosities of the filled and unfilled liquids, ϕ is the volume fraction of solids, and ϕ_f is the maximum volume fraction solids (at which $\eta_r = \infty$). The parameter ϕ_f is a function of the particle packing, and for uniform sized spheres is 0.74 by theory.

(U) Measurements of the viscosities of monodispersed suspensions fit an equation of the form proposed by Eilers with $\phi_f = 0.605$ which is approximately the theoretical for orthorhombic packing.

c. Similarity of Viscosity and Modulus of Filled Systems (U)

(U) The use of Eilers relation with the viscosity (η) replaced by Young's modulus (E)[9] has been proposed for the analogou[illegible]lastic problem of rubbers containing fillers. Some success was achieved by [illegible]mith[10] in application of an equation of the Eilers type to solid propellants.

(U) Therefore, the best packing of particles of different sizes will give a slurry with the lowest viscosity and for a given solids content will give a propellant with the lowest modulus. The maximum loading that such a packing would allow must, of course, be determined by its effect in a propellant system.

d. Effect of Particle Size Distribution on Viscosity (U)

(U) The use of particles of different size allows much more efficient packing of particles. Horsfield[11] calculated that a suspension with a solids concentration of 85.1% by volume is possible by use of particles of five different sizes.

(U) A number of investigators have experimentally studied suspension of bimodal distributions of solids up to 74% by volume. These studies show that the viscosity of concentrated suspensions could decrease markedly if the particle size ratio and relative amounts of small to large spheres were chosen properly.

e. Approach (U)

(U) The approach to more highly loaded solid propellants consisted of two distinct steps. The first involved the determination of the blends of available oxidizer particle sizes which gave a slurry with a minimum viscosity (best packing of particles). The second step was the determination of the maximum solids loading which were achieved with the blend determined in the first step.

f. Particle Sizes (U)

(U) Some available particle sizes of NH_4ClO_4, with the exception of 3-9 μ particles which were used as received, were screened to a narrower range of particle sizes for a study of the effect of particle size on the relative viscosity of a slurry.

(U) Screens were stacked as indicated in Table XXXIV and vibrated for approximately a half hour. The oxidizer remaining on each of the screens was weighed and the sizes to be used were separated. The oxidizers used were 3-9μ, 43-104μ, 104-250μ, and 250-495μ. These will be referred to as monoblended systems.

Table XXXIV

SCREENING OF NH_4ClO_4 INTO NARROW PARTICLE SIZE DISTRIBUTIONS (U)

Tyler Sieve No.	Sieve Opening Size μ	NH_4ClO_4 Initial Particle Blend: +48 % of Total[a]	+48 % of Total[a]	Unground % of Total[a]	Slow-Speed % of Total[a]	Slow-Speed % of Total[a]
10	1650	0.0	0.0	-[b]	-[b]	-[b]
16	991	0.033	0.0	-	-	-
20]c	833]c	0.027	0.0	-	-	-
32]	495]	7.52	15.60	-	-	-
48]c	297]c	89.80	80.90	15.0	-	0.67
60]	250]	3.19	2.68	15.7	6.64	4.83
100]c	149]c	-[b]	-[b]	43.2	49.4	40.8
150]	104]	-	-	17.5	20.1	22.30
200]c	74]c	-	-	4.72	11.2	12.05
325]	43]	-	-	1.85	8.4	11.55

[a]% retained on screen. [b]Dashes indicate screens not used.
[c]Parantheses indicate particle sizes combined.

(U) The particle size distribution by sieve analysis and the average particle size for each monoblended system is given in Table XXXV. The particle size distribution of the fine grind is 3-9μ with an average of 6μ.

Table XXXV

PARTICLE SIZE DISTRIBUTION AND AVERAGE PARTICLE SIZE OF NH_4ClO_4 USED FOR SLURRY VISCOSITY STUDIES (U)

Tyler Sieve No.	Sieve Opening Size, μ	Distribution %	Average Particle Size, μ
32	495	34	
35	420	32	419
42	350	29	
48	297	5	
65	210	29	
100	149	31	
150	105	15	148
200	75	11	
325	44	9	
765	-	5	
150	105	27	
200	75	36	71.2
325	44	36	

g. Viscosity Measurements with the Haake Rotovisko Viscometer (U)

(U) The viscosity measurements made with a Haake Rotovisko (Type RV) viscometer equipped with a multiple measuring head (50-500) and the Haake Circulator (Type RBD) at 30°C were consistent up to a volume fraction of solids loading of approximately 0.45 depending on the oxidizer system. At higher solids loadings the measured viscosities were lower than the values which would be expected from the extrapolated curve of relative viscosity (η_r) vs volume fraction of solids loading (Ø).

h. Viscosity Measurements with the Brookfield Synchro-Lectric Viscometer (U)

(U) Viscosities were determined with a Brookfield Synchro-Lectric Viscometer (Type HBF) in an effort to obtain accurate measurements at

the higher solids loading and as a check on the values obtained using the Haake Rotovisko viscometer. The Brookfield measurements were consistently higher than those obtained using the Haake Rotovisko viscometer (Figure 34). With the standard Brookfield spindles the viscosities fell below the extrapolated values at about 0.55 volume fraction solids due to the thixotropic nature of the slurry (Figures 35-38). More accurate measurements were made in the higher ranges using the Brookfield Heliopath Stand and the T-shaped spindle. With the higher viscosity measurements the determination of the maximum solids loading at infinite viscosity for each blend by extrapolation of the plot $1/(\eta_r^{\frac{1}{2}}-1)$ vs $1/\phi$ became more accurate. The Haake circulation bath (Type RBD) was used to maintain a standard temperature of 30°C.

i. Viscosity of Oxidizer Blends (U)

(U) The monoblend NH_4ClO_4 systems were blended and the relative viscosities of slurries in Oronite 6 were determined. The blend compositions are summarized in Table XXXVI, and the viscosity data are shown in Table XXXVII and Figures 35-47.

Table XXXVI

COMPOSITION AND AVERAGE PARTICLE SIZE OF NH_4ClO_4 BLENDS USED FOR SLURRY VISCOSITY STUDIES (U)

Blend No.	Composition, Wt% of Average Particle Size, μ: 6	71.2	148	419	Average Particle Size, μ	Mean Deviation[a]
1	-	-	50.00	50.00	283	136
2	-	50.00	-	50.00	245	173
3	50.00	-	-	50.00	211	220
4	-	33.33	33.33	33.33	213	139
5	33.33	-	33.33	33.33	190	159
6	33.33	33.33	-	33.33	165	168
7	-	-	84.16	15.48	180	86.7
8	-	68.72	-	31.28	180	148
9	57.87	-	-	42.13	180	201
10	-	56.94	14.35	28.71	180	138
11	45.37	-	18.21	36.42	180	176
12	41.43	19.52	-	39.05	180	186
13	35.80	-	32.10	32.10	180	157
14	49.12	-	12.72	38.16	180	184
15	22.21	-	51.86	25.93	180	130
16	13.00	-	65.25	21.75	180	112

[a]This indicates the spread of the blend, but has little meaning for these non-Gaussian distributions.

RELATIVE VISCOSITIES OF NH_4ClO_4 - ORONITE 6 SLURRIES MEASURED WITH BROOKFIELD VISCOMETER AND HAAKE ROTOVISKO VISCOMETER

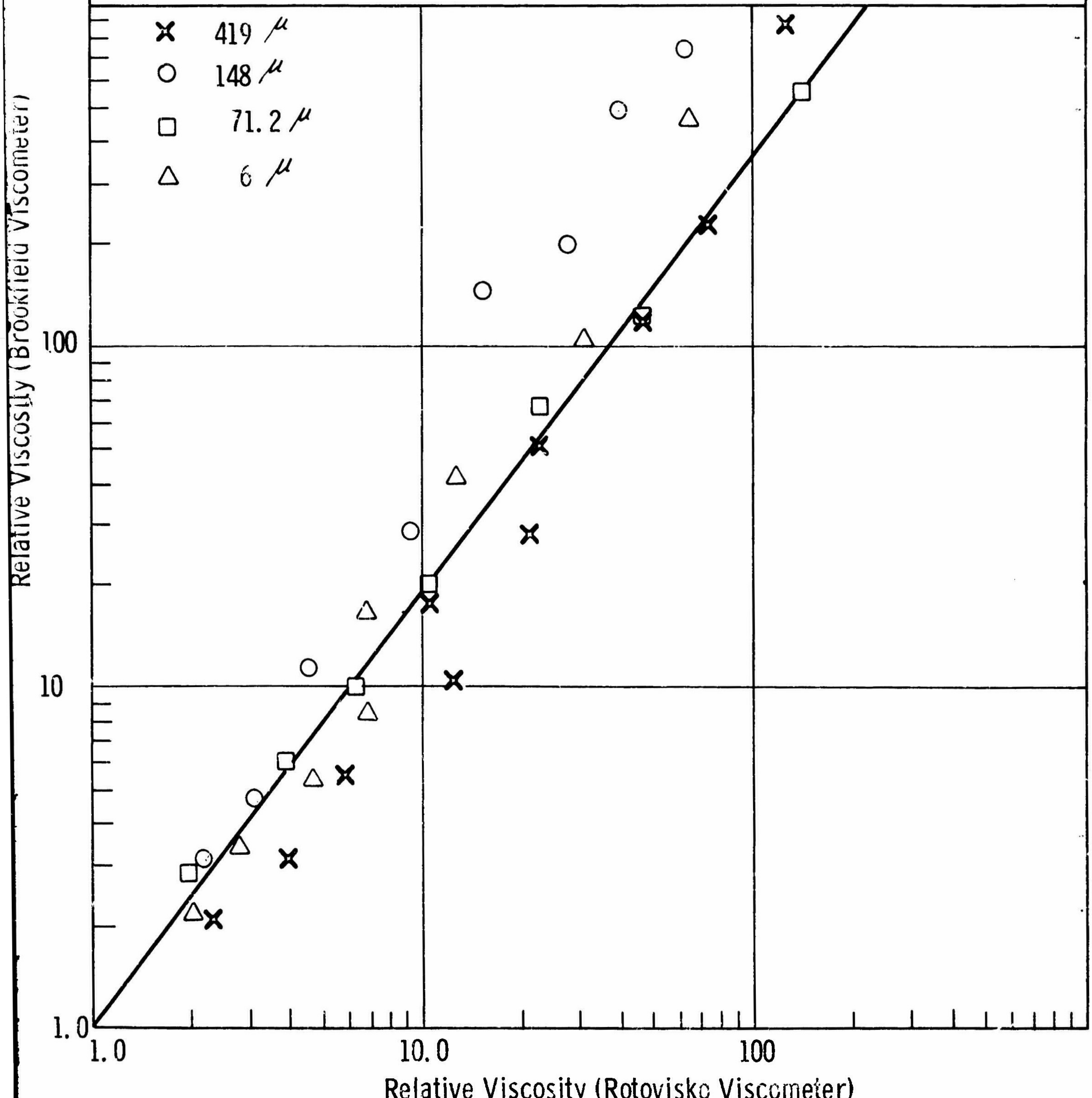


Figure 34

Table XXXVII

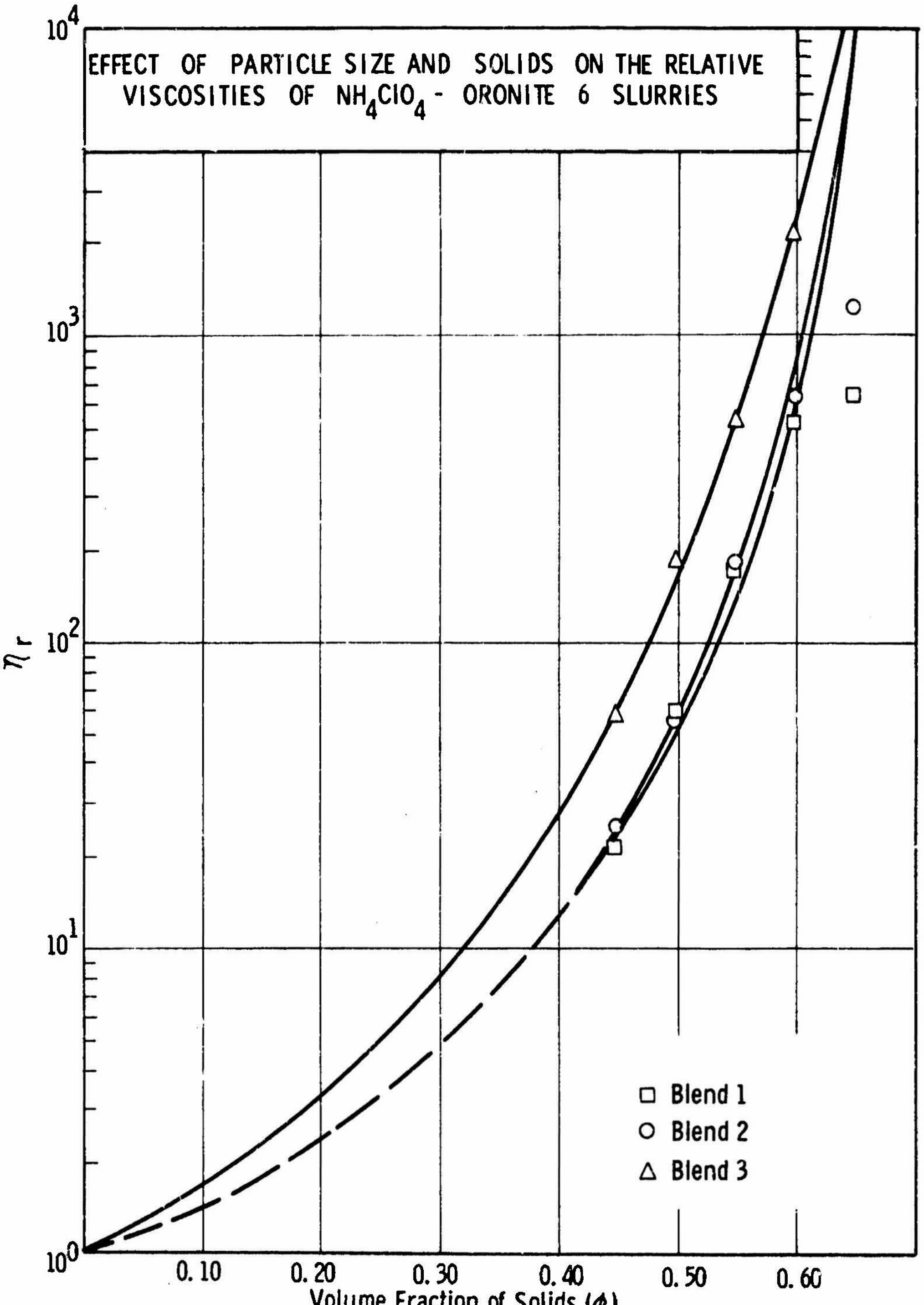
VISCOSITIES OF NH_4ClO_4-ORONITE 6 SLURRIES[a] AT 30°C (U)

Blend[a] No.	Vol. Fract. (Ø)	1/Ø	$Ø_f$	$\eta_{cp} x10^3$	η_r	$\eta_r^{1/2}$	$\eta_r^{1/2}-1$	$\frac{1}{\eta_r^{1/2}-1}$
1	0.45	2.22	0.667	0.864	21.6	4.65	3.65	0.274
	0.50	2.00		2.36	59.0	7.68	6.68	0.150
	0.55	1.82		6.80	170.0	13.03	12.03	0.0831
	0.60	1.67		20.2	504.0	22.46	21.46	0.0466
	0.65	1.54		24.3	608.0	24.62	23.62	0.0423
2	0.45	2.22	0.649	0.992	24.8	4.98	3.98	0.251
	0.50	2.00		2.18	54.4	7.35	6.35	0.157
	0.55	1.82		7.26	181.6	13.47	12.47	0.0803
	0.60	1.67		25.0	624.0	25.00	24.00	0.0416
	0.65	1.54		48.3	1208.0	34.78	33.78	0.0296
3	0.45	2.22	0.602	2.28	57.0	7.46	6.46	0.155
	0.50	2.00		5.94	148.4	12.19	11.19	0.0894
	0.55	1.82		21.1	528.0	22.96	21.96	0.0456
	0.60	1.67		86.7	2168.0	46.60	45.60	0.0219
4	0.45	2.22	0.725	1.54	38.4	6.19	5.19	0.193
	0.50	2.00		4.68	117.0	10.81	9.81	0.102
	0.55	1.82		19.4	484.8	22.00	21.00	0.0477
	0.60	1.67		43.2	1080.0	32.85	31.85	0.0314
	0.65	1.54		128	3200.0	56.52	55.52	0.018
5	0.45	2.22	0.641	1.96	49.0	7.0	6.0	0.167
	0.50	2.00		5.38	134.4	11.60	10.60	0.094
	0.55	1.82		14.5	361.6	19.02	18.02	0.0555
	0.60	1.67		75.2	1880.0	43.40	42.40	0.0236
6	0.45	2.22	0.641	4.54	113.6	10.63	9.63	0.104
	0.50	2.00		13.5	337.6	18.38	17.38	0.0576
	0.55	1.82		35.2	880.0	29.62	28.62	0.0349
	0.60	1.67		212	5300.0	72.70	71.70	0.0140
7	0.45	2.22	0.658	2.800	70	8.38	7.38	0.136
	0.50	2.00		19.8	496	22.30	21.30	0.0470
	0.55	1.82		37.4	936	30.60	29.60	0.0337
	0.60	1.67		240	6000	77.60	76.60	0.0131
	0.63	1.54		320	8000	89.50	88.50	0.0113
8	0.45	2.22	0.637	9.20	230	15.2	14.2	0.0704
	0.50	2.00		29.4	736	27.2	26.2	0.0382
	0.55	1.82		86.4	2160	46.6	45.6	0.0219
	0.60	1.67		435	10900	104.4	103.4	0.00967

[a]Blend composition given in Table XXXVI.

Table XXXVII (Cont)

Blend No.	Vol. Fract. (ϕ)	$1/\phi$	ϕ_f	$\eta_{cp} \times 10^3$	η_r	$\eta_r^{\frac{1}{2}}$	$\eta_r^{\frac{1}{2}}-1$	$\frac{1}{\eta_r^{\frac{1}{2}}-1}$
9	0.45	2.22	0.667	5.20	130	11.4	10.4	0.0962
	0.50	2.00		11.5	288	17.0	16.0	0.0625
	0.55	1.82		27.2	680	26.1	25.1	0.0398
	0.60	1.67		83.2	2080	45.6	44.6	0.0224
	0.65	1.54		204	51000	225.8	224.8	0.00445
10	0.45	2.22	0.662	5.40	126	11.23	10.23	0.098
	0.50	2.00		25.9	648	25.50	24.50	0.048
	0.55	1.82		65.6	1640	40.50	39.50	0.0253
	0.60	1.67		147	3675.5	60.61	59.51	0.0168
	0.62	1.61		352	8800.0	93.80	92.80	0.0108
11	0.45	2.22	0.671	9.76	244	15.61	14.61	0.0683
	0.50	2.00		23.7	592	24.40	23.40	0.0428
	0.55	1.82		57.6	1440	37.90	36.90	0.0272
	0.60	1.67		176	4400	66.40	65.40	0.0153
12	0.45	2.22	0.645	7.20	180	13.42	12.42	0.0802
	0.50	2.00		18.2	456	21.40	20.40	0.0491
	0.55	1.82		49.6	1240	35.20	34.20	0.0293
	0.60	1.67		230	5760	75.90	74.90	0.0134
13	0.45	2.22	0.686	8.16	204	14.28	13.28	0.0754
	0.50	2.00		21.1	528	22.96	21.96	0.0456
	0.55	1.82		32.0	800	28.30	27.30	0.0366
	0.60	1.67		96.0	2400	49.00	48.00	0.0208
	0.63	1.59		205	5120	71.60	70.60	0.0142
14	0.45	2.22	0.642	9.92	248	15.75	14.75	0.0678
	0.50	2.00		23.4	584	24.04	23.04	0.0433
	0.55	1.82		60.8	1520	39.00	38.00	0.0263
	0.60	1.67		346	8640	93.10	92.10	0.0109
15	0.45	2.22	0.676	2.80	70	8.38	7.38	0.0136
	0.50	2.00		11.8	296	17.24	16.24	0.0613
	0.55	1.82		27.2	680	26.15	25.15	0.0392
	0.60	1.67		67.2	1680	41.00	40.00	0.0250
	0.63	1.59		99.2	2480	49.80	48.80	0.0205
16	0.45	2.22	0.662	2.64	66	8.13	7.13	0.140
	0.50	2.00		11.0	276	16.62	15.62	0.0640
	0.55	1.82		25.6	640	25.40	24.40	0.0410
	0.60	1.67		86.4	2160	46.50	45.50	0.0220
	0.63	1.59		131	3280	57.27	56.27	0.0177



EFFECT OF PARTICLE SIZE AND SOLIDS ON THE RELATIVE VISCOSITIES OF NH4ClO4 - ORONITE 6 SLURRIES
10^4
10^3
10^2
10^1
10^0
ηr
0.10
0.20
0.30
0.40
0.50
0.60
Volume Fraction of Solids (φ)
□ Blend 1
○ Blend 2
△ Blend 3

Figure 35

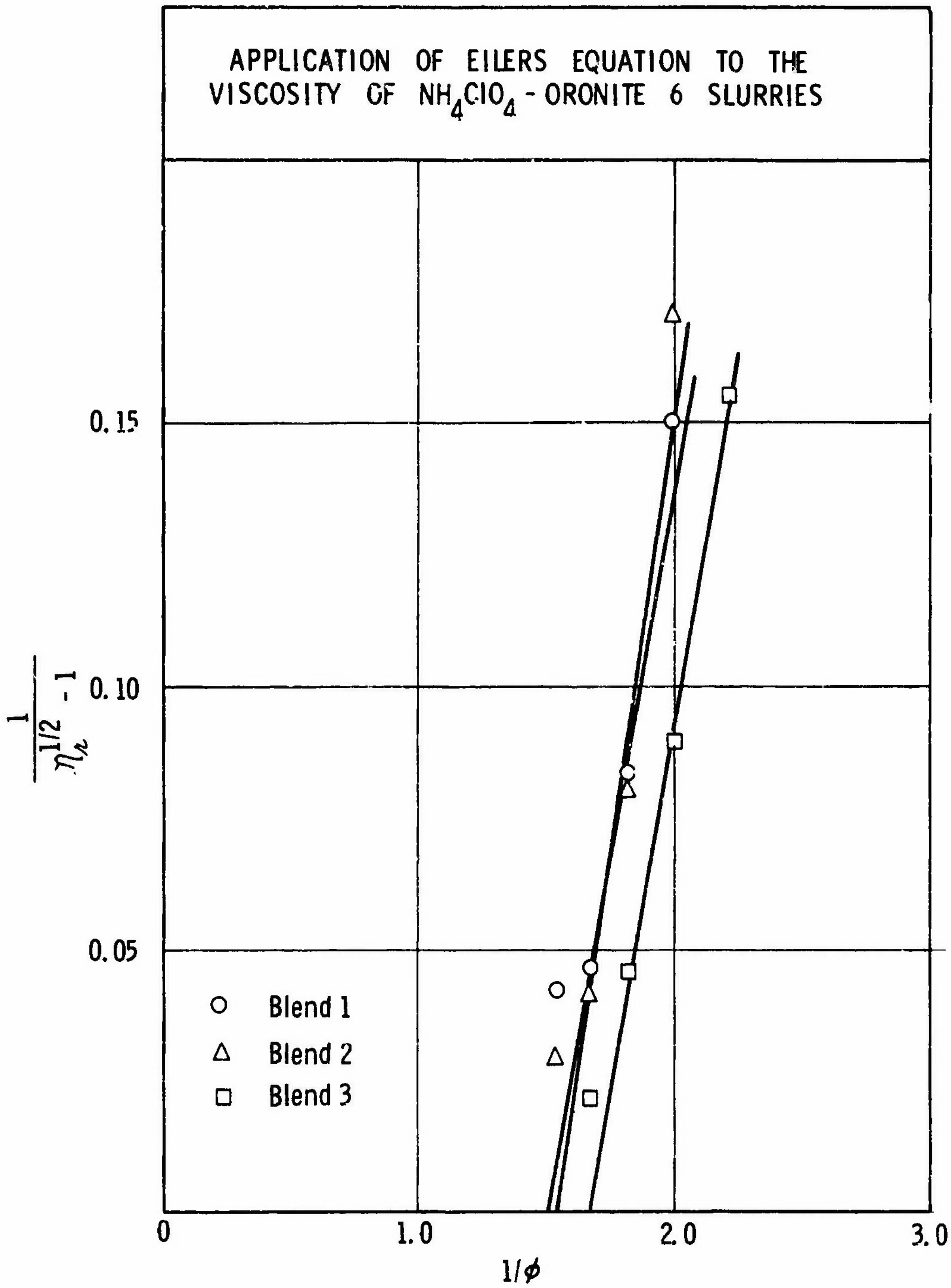

APPLICATION OF EILERS EQUATION TO THE
VISCOSITY OF NH_4ClO_4 - ORONITE 6 SLURRIES
0.15
0.10
0.05
$\frac{1}{\eta_r^{1/2}} - 1$
Blend 1
Blend 2
Blend 3
0
1.0
2.0
3.0
$1/\phi$

Figure 36

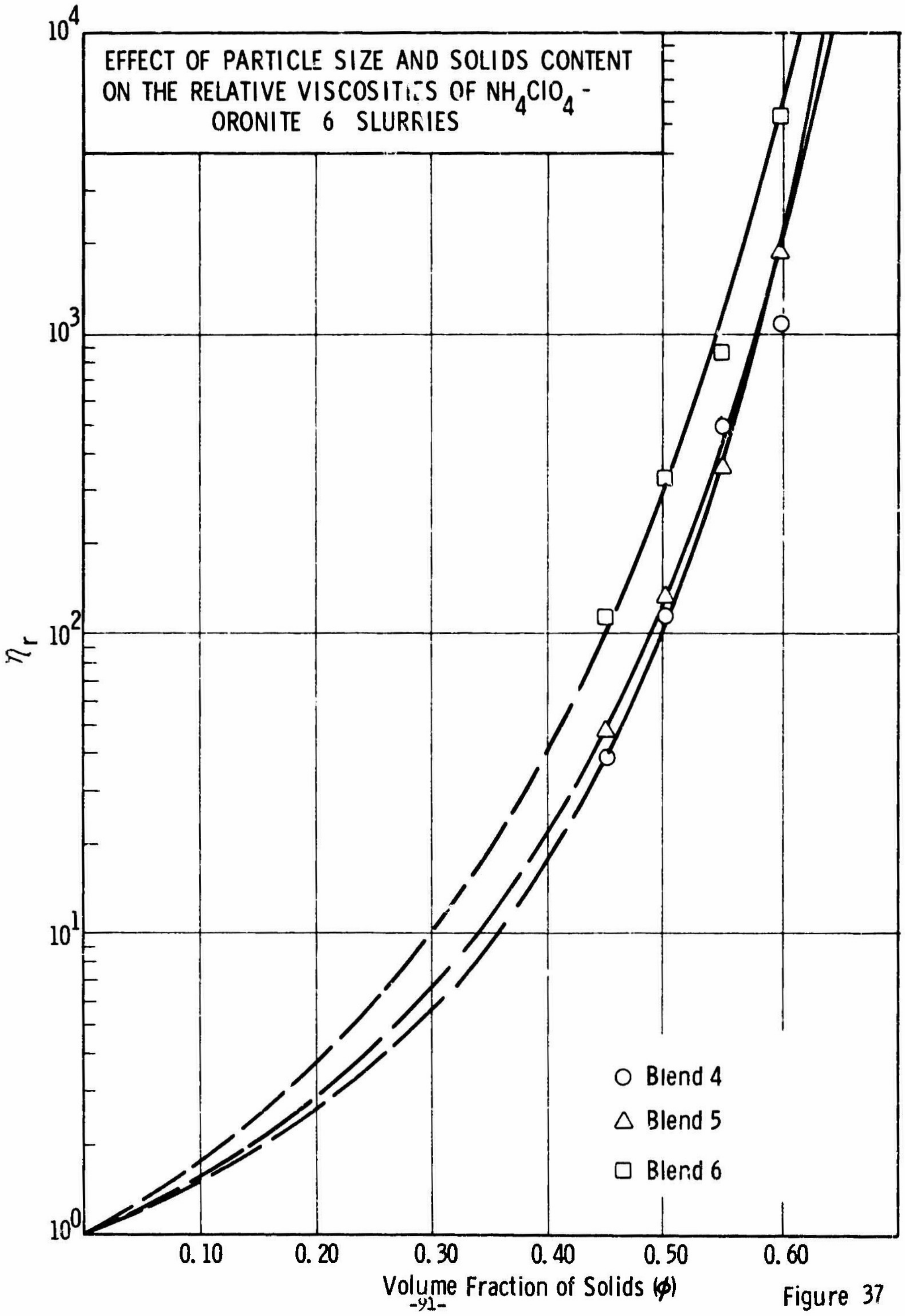

EFFECT OF PARTICLE SIZE AND SOLIDS CONTENT ON THE RELATIVE VISCOSITIES OF NH_4ClO_4 - ORONITE 6 SLURRIES
10^4
10^3
10^2
10^1
10^0
η_r
0.10
0.20
0.30
0.40
0.50
0.60
Volume Fraction of Solids (ϕ)
○ Blend 4
△ Blend 5
□ Blend 6

Figure 37

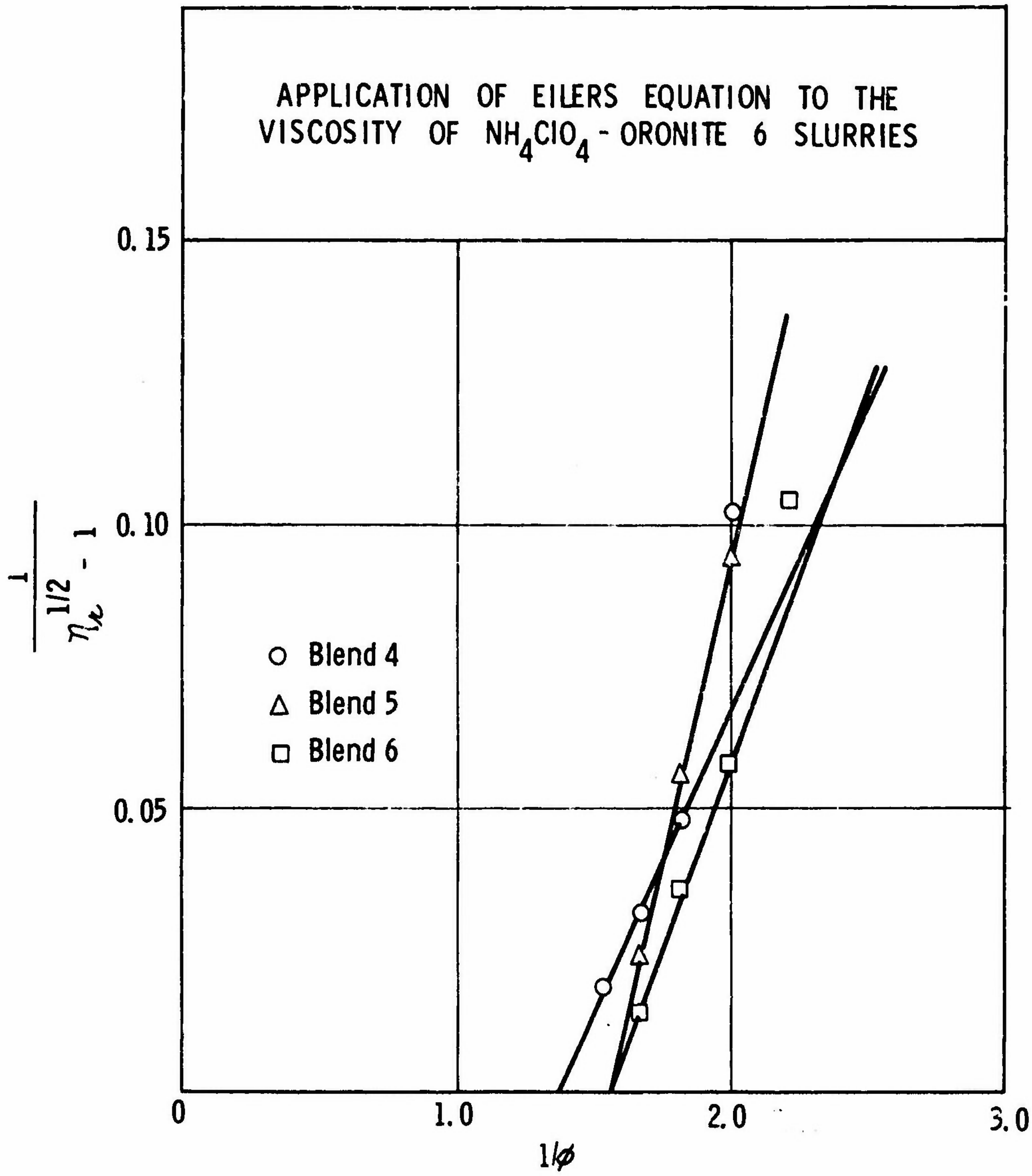

APPLICATION OF EILERS EQUATION TO THE VISCOSITY OF NH_4ClO_4 - ORONITE 6 SLURRIES
0.15
0.10
0.05
0
1.0
2.0
3.0
$1/\phi$
$\frac{1}{\eta_r^{1/2} - 1}$
Blend 4
Blend 5
Blend 6

Figure 38

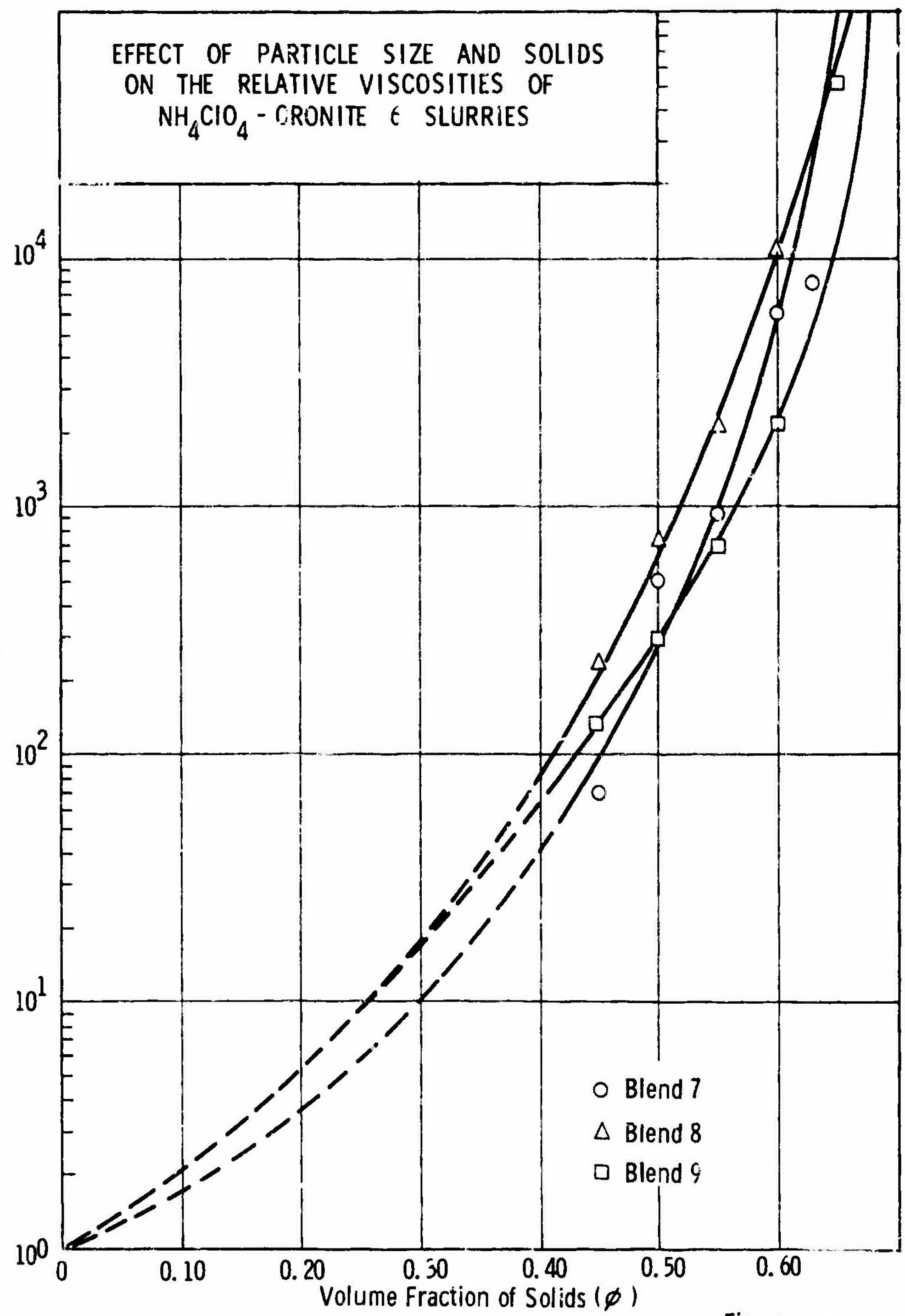

EFFECT OF PARTICLE SIZE AND SOLIDS ON THE RELATIVE VISCOSITIES OF NH_4ClO_4 - CRONITE 6 SLURRIES
10^4
10^3
10^2
10^1
10^0
η_r
0
0.10
0.20
0.30
0.40
0.50
0.60
Volume Fraction of Solids (ϕ)
○ Blend 7
△ Blend 8
□ Blend 9

Figure 59

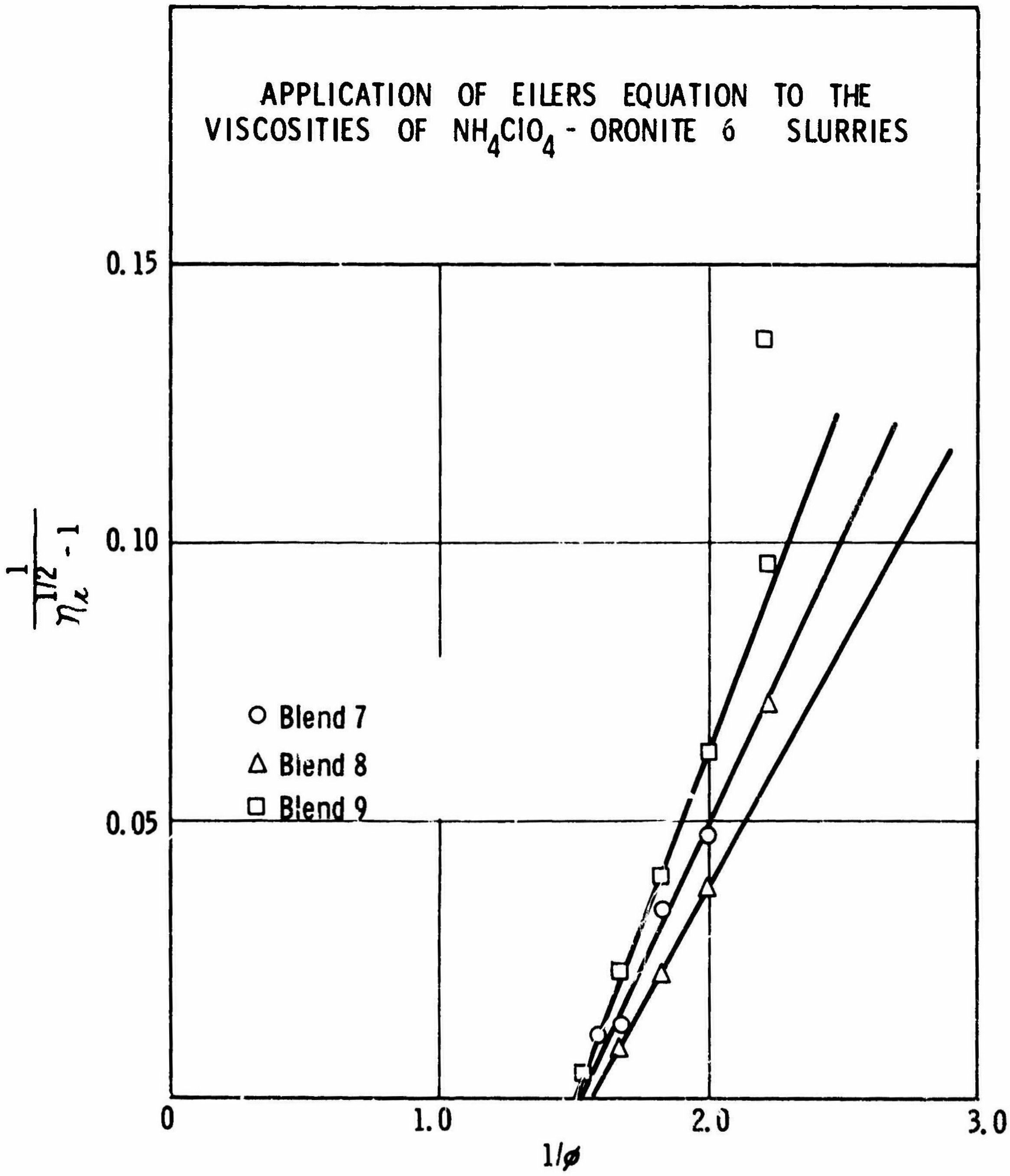

APPLICATION OF EILERS EQUATION TO THE VISCOSITIES OF NH_4ClO_4 - ORONITE 6 SLURRIES
0.15
0.10
0.05
$\frac{1}{\eta_r^{1/2} - 1}$
Blend 7
Blend 8
Blend 9
0
1.0
2.0
3.0
$1/\phi$

Figure 40

UNCLASSIFIED

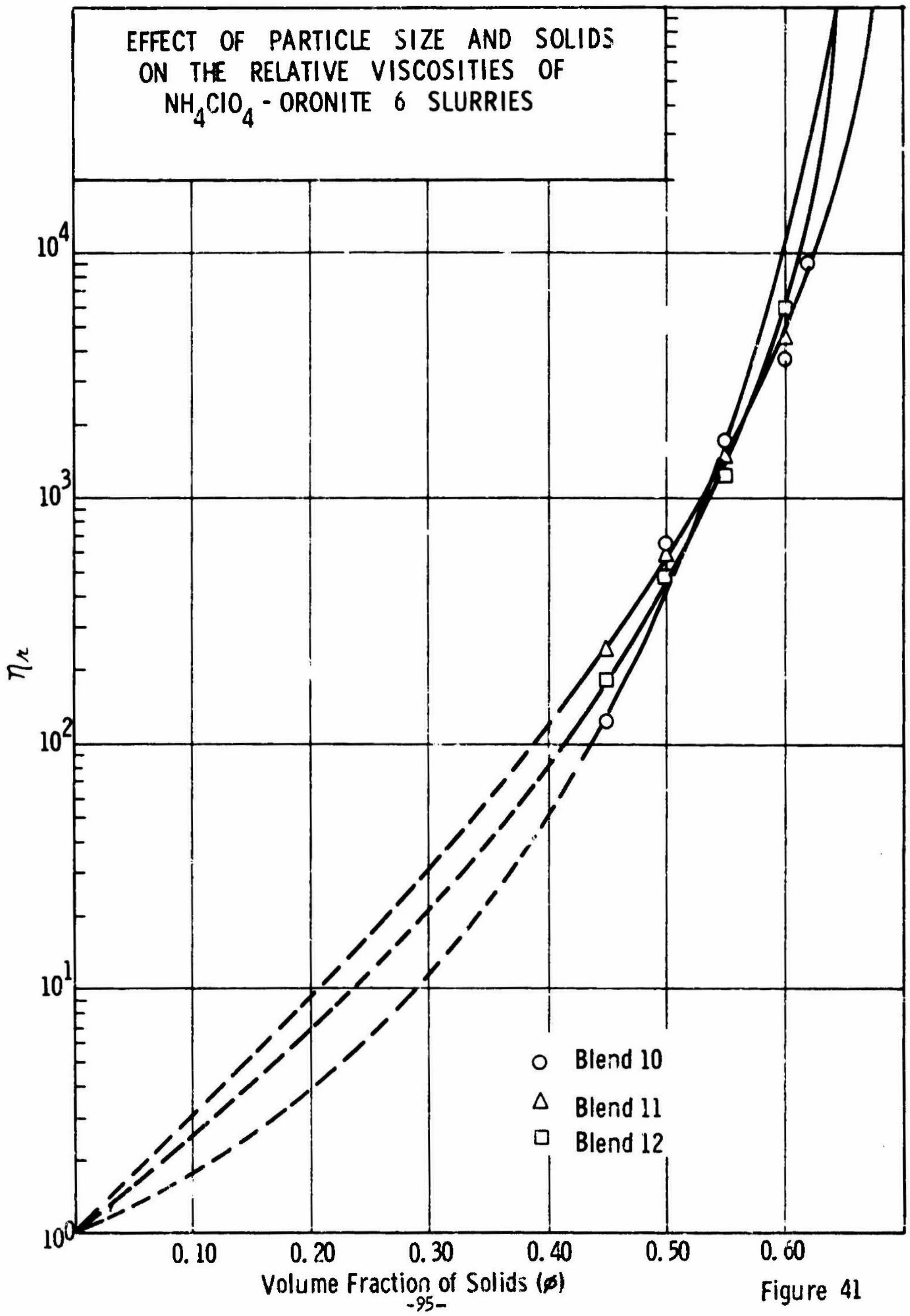
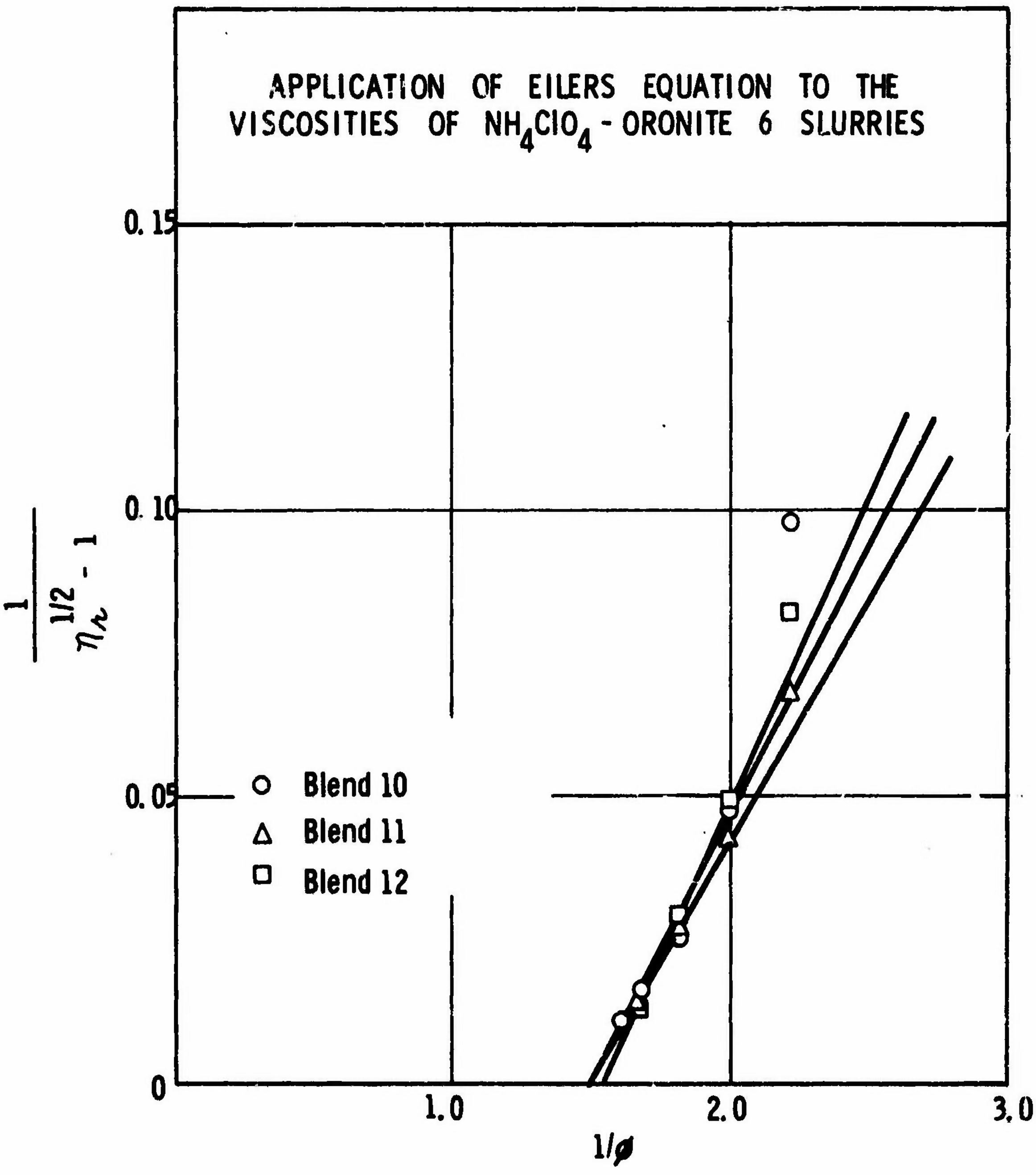


Figure 41

UNCLASSIFIED



APPLICATION OF EILERS EQUATION TO THE VISCOSITIES OF NH_4ClO_4 - ORONITE 6 SLURRIES
0.15
0.10
0.05
0
$\frac{1}{\eta_r^{1/2} - 1}$
Blend 10
Blend 11
Blend 12
1.0
2.0
3.0
1/ø

Figure 42

UNCLASSIFIED

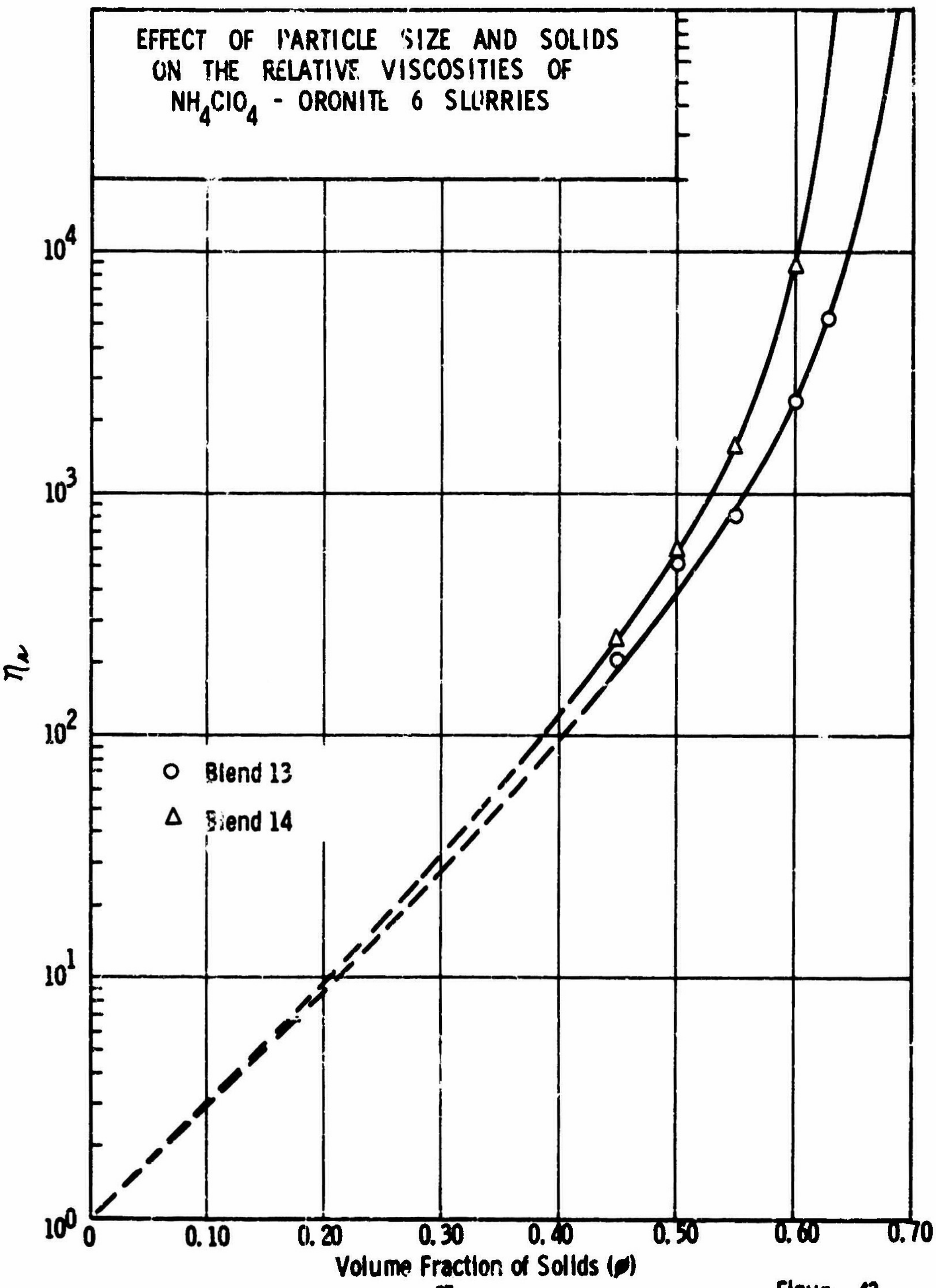
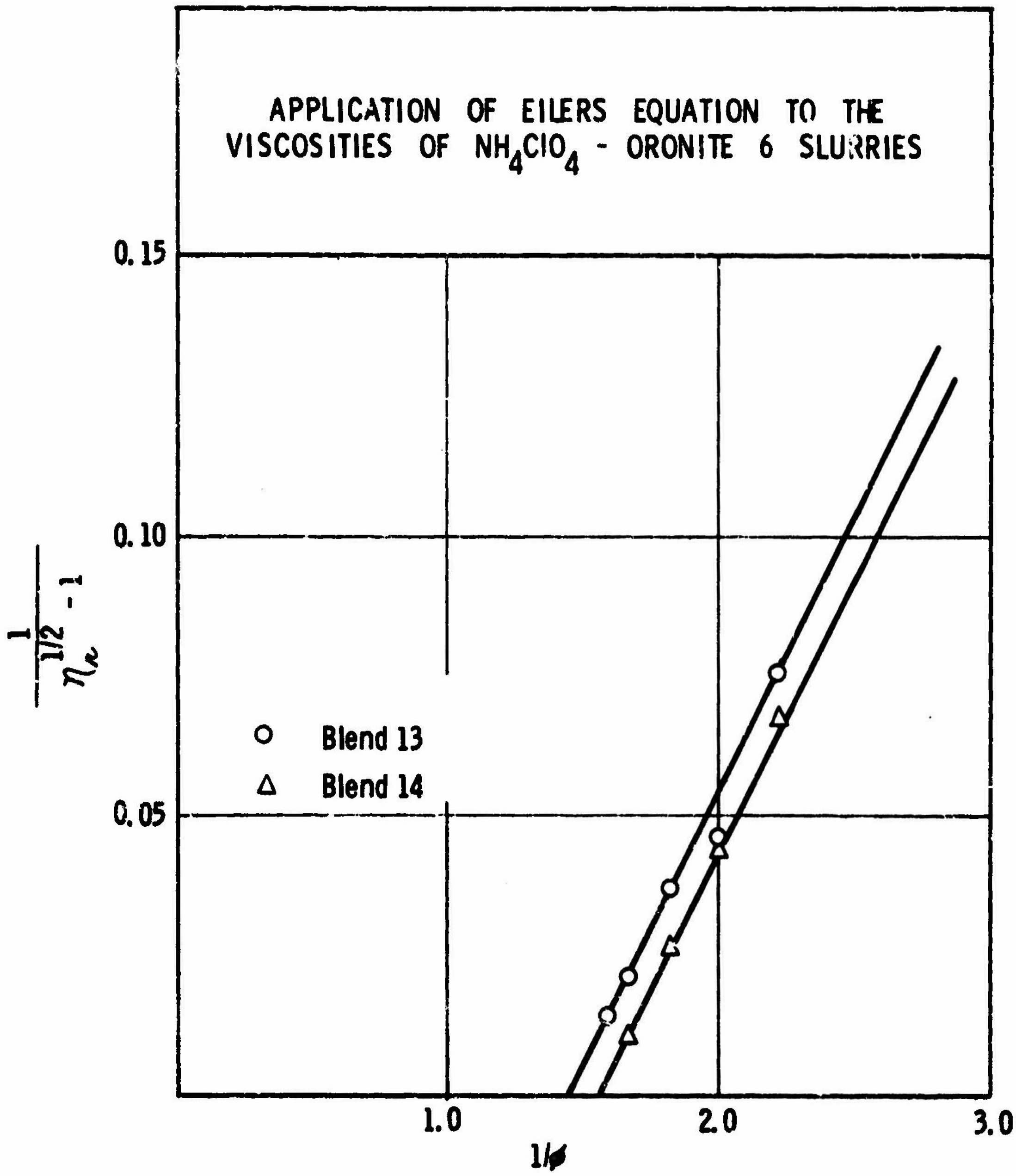


Figure 43



APPLICATION OF EILERS EQUATION TO THE VISCOSITIES OF NH_4ClO_4 - ORONITE 6 SLURRIES
0.15
0.10
0.05
$\frac{1}{\eta_r^{1/2} - 1}$
Blend 13
Blend 14
1.0
2.0
3.0
$1/\phi$

Figure 44

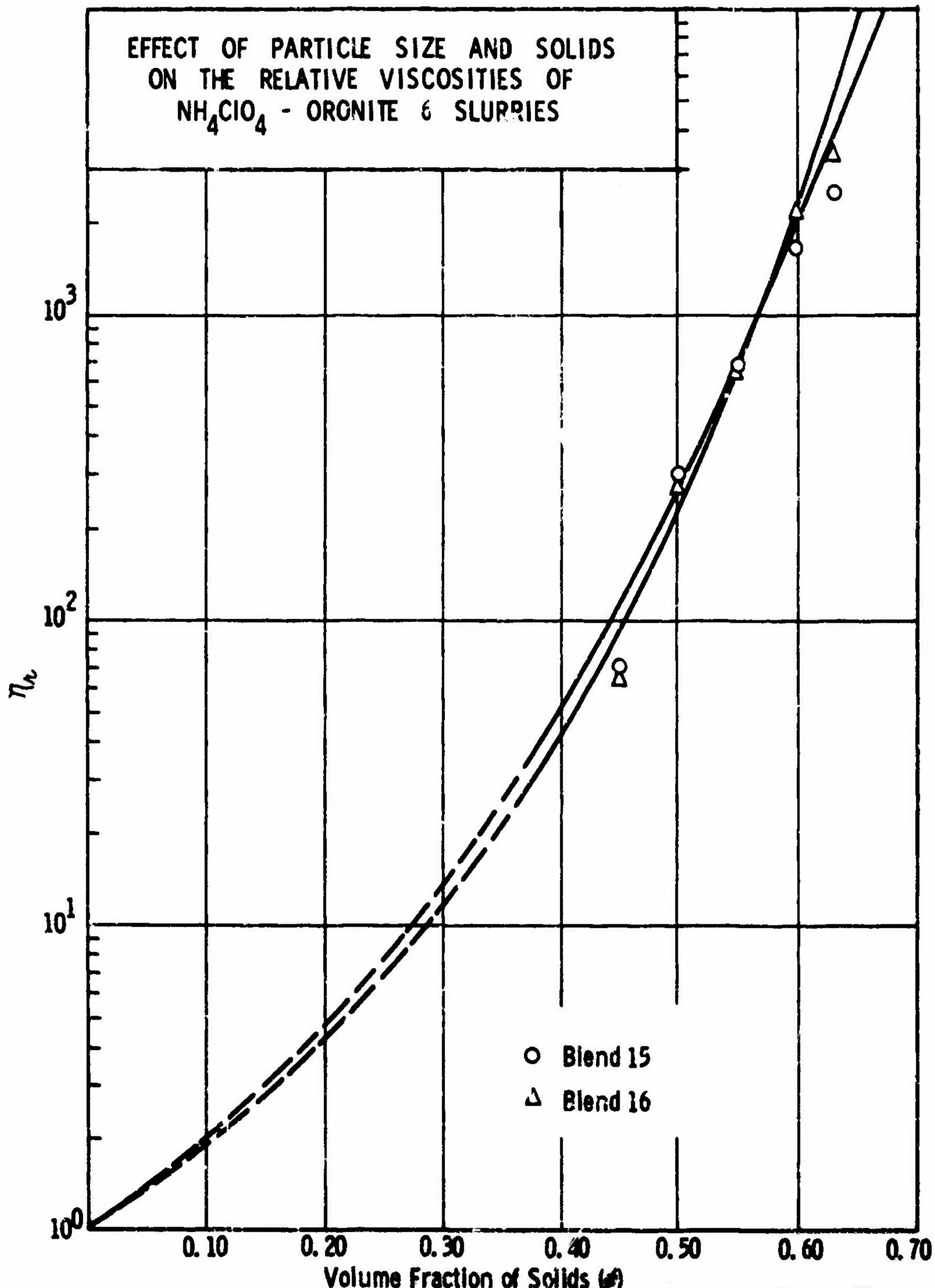

EFFECT OF PARTICLE SIZE AND SOLIDS ON THE RELATIVE VISCOSITIES OF NH_4ClO_4 - ORONITE 6 SLURRIES
η_r
10^3
10^2
10^1
10^0
0.10
0.20
0.30
0.40
0.50
0.60
0.70
Blend 15
Blend 16
Volume Fraction of Solids (φ)

Figure 45

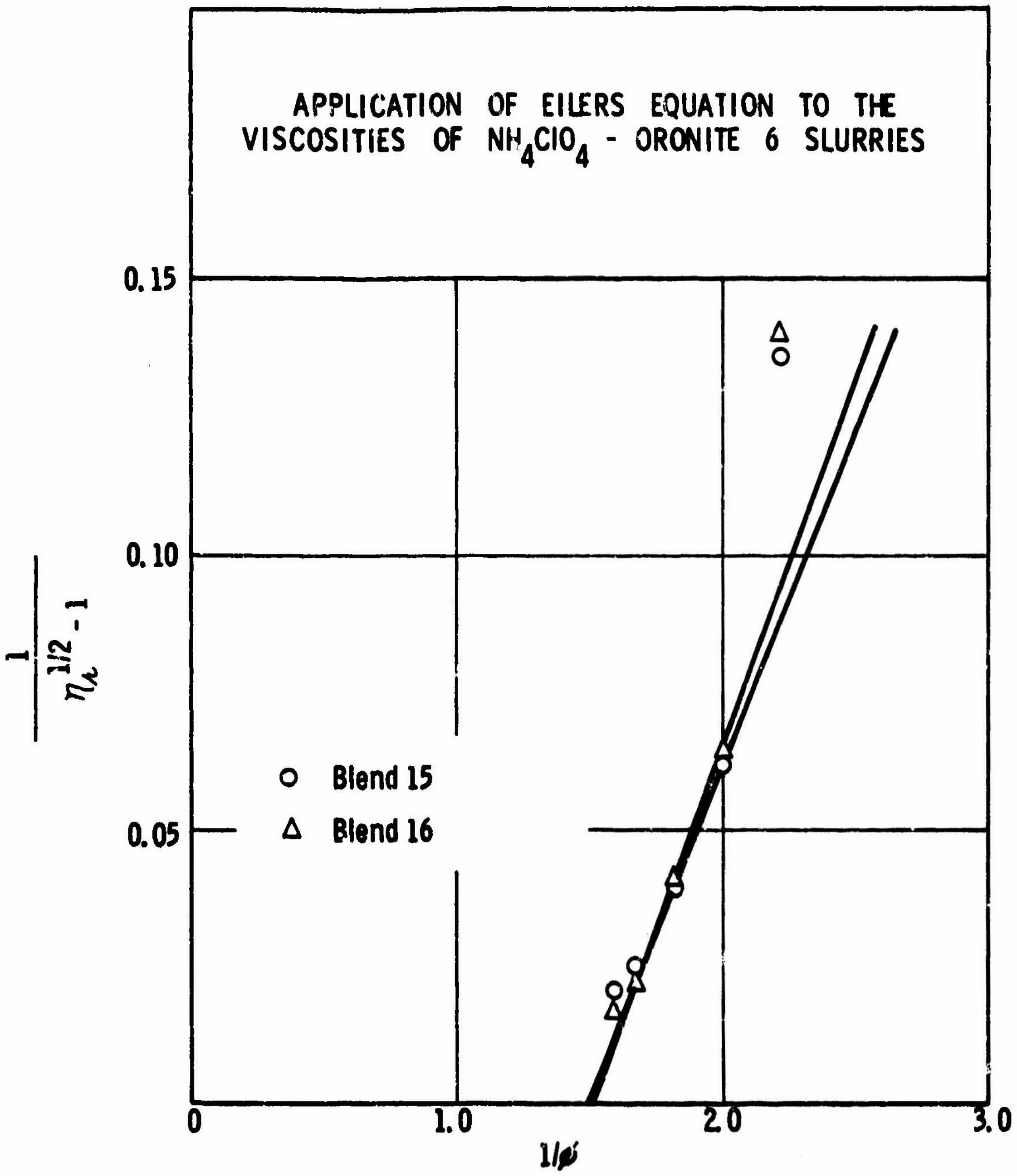

APPLICATION OF EILERS EQUATION TO THE VISCOSITIES OF NH_4ClO_4 - ORONITE 6 SLURRIES
0.15
0.10
0.05
0
1.0
2.0
3.0
$1/\phi$
$\frac{1}{\eta_r^{1/2} - 1}$
○ Blend 15
△ Blend 16

Figure 46

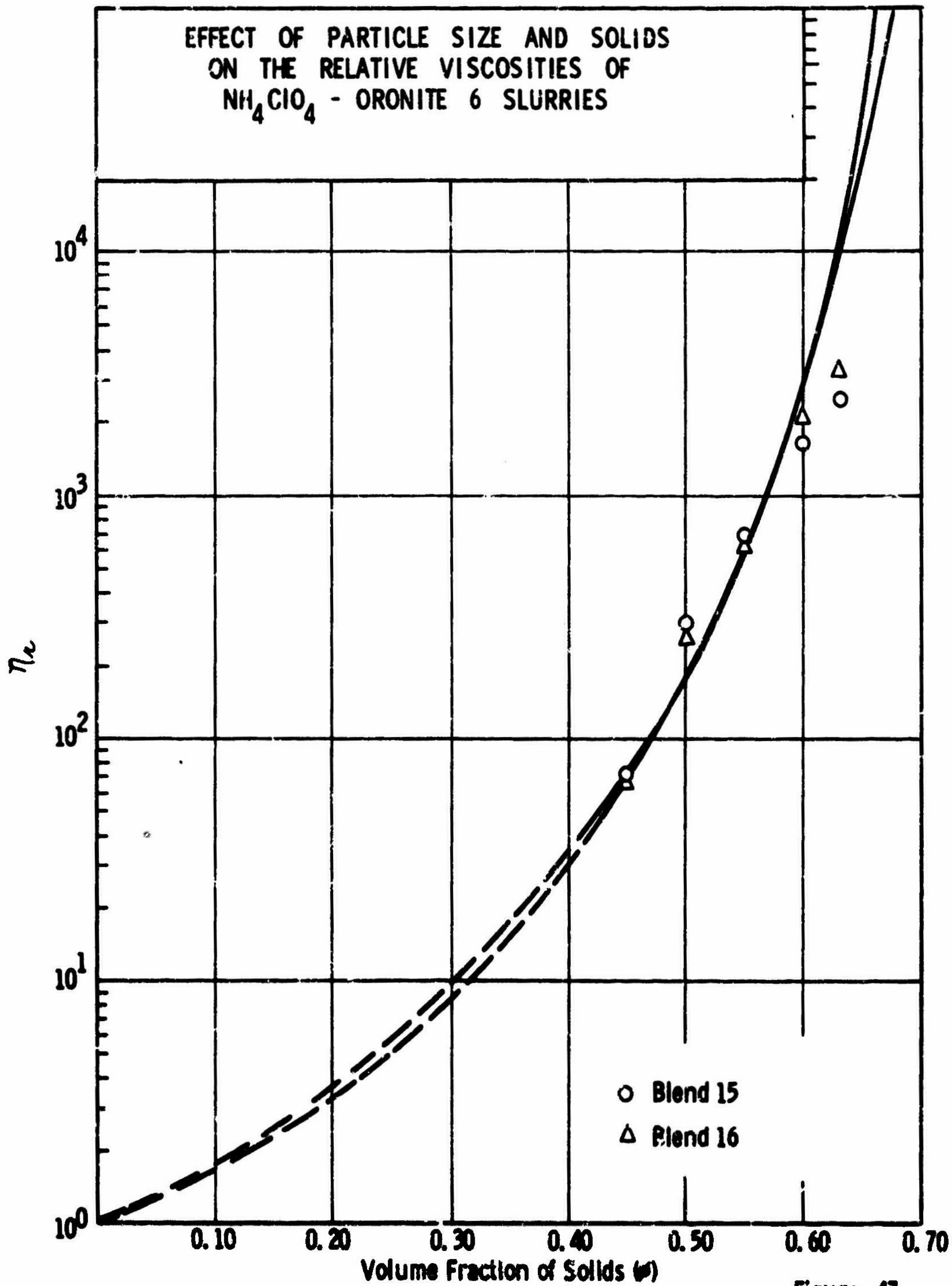

EFFECT OF PARTICLE SIZE AND SOLIDS
ON THE RELATIVE VISCOSITIES OF
NH4ClO4 - ORONITE 6 SLURRIES
10^4
10^3
10^2
10^1
10^0
0.10
0.20
0.30
0.40
0.50
0.60
0.70
Volume Fraction of Solids (φ)
Blend 15
Blend 16

Figure 47

(U) Blends 1-6, compositions of which are given in Table XXXVI were a series of bimodal and trimodal blends selected at random, the viscosities of which were measured to determine the viscosity differences between blends and the accuracy with which the viscosity could be measured. The data were consistent, and the viscosities of the blends were easily distinguishable with the exception of Blends 1 and 2, the viscosities of which were very close.

(U) An average particle size of 180μ was maintained in formulating blends 7-16 in order to maintain a useful burning rate range. Blends 7-12 were made up using various particle sizes to give the 180μ average. Blend 11, with a 2 to 1 ratio of the 419μ to 148μ particle size NH_4ClO_4, gave Oronite 6 slurries with the lowest relative viscosity. Blends 13-16 were then prepared to produce variants of Blend 11 with different ratios of the 419μ to 148μ particle size NH_4ClO_4, maintaining the 180μ particle size average.

(U) A plot of ϕ_f vs ratio of 419μ to 148μ particle sizes in the blend is given in Figure 48 including that for Blend 11. Blend 13 (1 to 1 ratio) had the highest ϕ_f and was used for propellant studies. Additional minor modifications in the blends were made in the course of the propellant studies.

j. Propellant Studies (U)

(U) This task progressed very well without serious technical problems. With the completion of the viscosity studies on slurries, the effort proceeded to propellant studies.

(U) A series of propellant batches was made on the 50-gram scale using the Atlantic Research Corp. horizontal mixer. The purpose of these studies was to determine mixing and casting properties at higher solids loading using Oxidizer Blend 13 (Table XXXVI). Mechanical properties of some of these propellants were determined (Table XXXVIII).

(U) Propellants 1 and 2 did not cure and the data are not reported. The 50-gram batches which contained C-1 at the higher solids loading and which were made on the small scale did not mix or cast well, so lecithin was used as a wetting agent. Most of these propellants mixed well when mixed from two to three hours and when the oxidizer was added slowly. Propellants 12 and 13 were duplicated on the 1-lb scale in the Baker-Perkins vertical mixer (Propellants 14 and 15). Mixing and casting were much improved on the larger scale.

(U) A 92% solids loaded propellant (Propellant 16) was made but after a three-hour mix cycle, the propellant was just barely mixed and not castable. The propellants made at 91% solids loading and at 135°F, mixed well in approximately 1.5 hours and were castable. The solids loading was limited to 91% and the mechanical properties were further optimized.

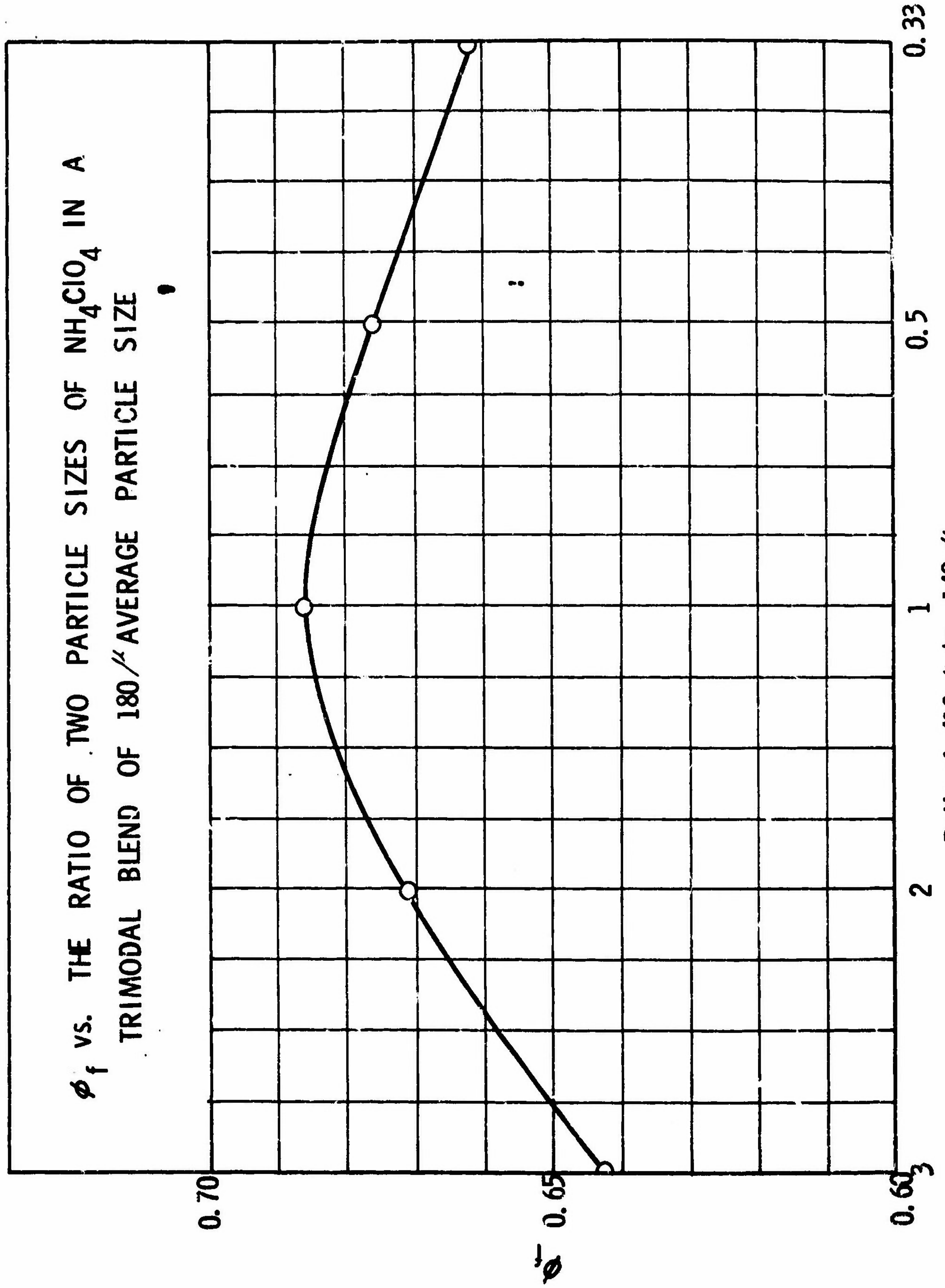

ϕ_f vs. THE RATIO OF TWO PARTICLE SIZES OF NH_4ClO_4 IN A
TRIMODAL BLEND OF 180μ AVERAGE PARTICLE SIZE
0.70
0.65
0.60
ϕ_f
3
2
1
0.5
0.33
Ratio of 419μ to 148μ

Figure 48

Table XXXVIII

MAXIMUM SOLIDS LOADED PROPELLANTS[a] (U)

Reference No.	Batch Size	Solids Loading (%)	Oxidizer Blend[b]	Aluminum[c] Weight, %	Aluminum[c] Size, μ	Wetting Agent	Amount (%)	Mix Temp (°F)	NCO/OH	HDI/CTI
3	50-gm	88	13	15.00	30-40	C-1	0.10	110	0.945	4.15
4	50-gm	90	13	15.34	30-40	C-1	0.10	110	0.945	4.17
5	50-gm	88	13	15.00	30-40	C-1	0.10	110	1.00	4.00
6	50-gm	90	13	15.34	30-40	C-1	0.10	110	1.00	4.00
7	50-gm	90	13	15.34	30-40	C-1	0.10	125	1.00	4.00
8	50-gm	90	13	15.34	30-40	lec.	0.10	125	1.00	4.00
9	50-gm	90	13	15.34	30-40	C-1	0.20	125	1.00	4.00
10	50-gm	91.1	13	15.68	30-40	Lec.	0.10	125	1.00	4.00
11	50-gm	91.1	13	15.68	30-40	Lec.	0.20	125	1.00	4.00
12	50-gm	91.1	13	15.00	30-40	Lec.	0.20	125	1.00	4.00
13	50-gm	91.1	13	12.00	30-40	Lec.	0.20	125	1.00	4.00
14	1-lb	91.1	13	15.00	30-40	Lec.	0.20	135	1.00	4.00
15	1-lb	91.1	13	12.00	30-40	Lec.	0.20	135	1.00	4.00
16	1-lb	92	13	12.00	30-40	Lec.	0.20	135	1.05	4.00
17	1-lb	91	13	12.00	30-40	Lec.	0.20	135	1.05	4.00
18	1-lb	91	13	12.00	30-40	Lec.	0.20	135	1.05	4.25
19	1-lb	91	13	12.00	40-50	Lec.	0.20	135	1.05	4.25
20	1-lb	91	13	12.00	8-14	Lec.	0.20	135	1.05	4.25
21	1-lb	91	Std.-13	12.00	40-50	Lec.	0.20	135	1.05	4.25
22	1-lb	91	13	12.00	40-50	C-1	0.10	135	1.05	4.25
23	1-lb	91	Std.-13	12.00	40-50	Aerosol TR	0.20	135	1.05	4.25
24	1-lb	91	Std.-13	12.00	40-50	Aerosol TR	0.20	135	1.05	4.25
25	1-lb	91	Std.-13	12.00	40-50	C-1	0.10	135	1.05	4.25
26	1-lb	91	Std.-13	12.00	40-50	C-1	0.10	135	1.05	4.25
27	10-lb	91	Std.-13	12.00	40-50	C-1	0.10	135	1.05	4.25
28	1-lb	91	Dried Std.-13	12.00	40-50	C-1	0.10	135	1.05	4.25
29	60-lb	91	Std.-13	12.00	40-50	C-1	0.10	135	1.05	4.25

[a] See Footnotes on following page

Table XXXVIII

M SOLIDS LOADED PROPELLANTS[a] (U)

tting gent	Amount (%)	Mix Temp (°F)	NCO/OH	HDI/CTI	Plastimeter Reading	Casta- bility	Mechanical Properties at 77°F σ_{nm} psi	σ_{nb} psi	ϵ_{nm} %	ϵ_{nb} %	E_0 psi
C-1	0.10	110	0.945	4.15	19.5/21.5	good	56.3	52.5	23.6	28.5	359
C-1	0.10	110	0.945	4.17	20.0/21.0	good	52.1	49.0	21.7	26.5	352
C-1	0.10	110	1.00	4.00	19.5/21.0	good	142.5	132.5	13.2	17.8	1695
C-1	0.10	110	1.00	4.00	15.5/16.5	poor	162.8	159.1	13.3	14.7	[illegible]
C-1	0.10	125	1.00	4.00	17.0/18.5	poor	106.5	103.9	9.1	10.5	1665
lec.	0.10	125	1.00	4.00	21.5/22.5	good	55.7	45.7	11.4	19.7	738
C-1	0.20	125	1.00	4.00	Batch was not castable - scrapped.						
Lec.	0.10	125	1.00	4.00	15.5/18.0	poor	54.0	26.0	7.1	11.9	1006
Lec.	0.20	125	1.00	4.00	16.5/18.5		- scrapped.				
Lec.	0.20	125	1.00	4.00	17 /19.0	poor	43.7	22.0	12.3	16.6	464
Lec.	0.20	125	1.00	4.00	17.0/18.5	poor	49.2	43.7	12.8	16.7	518
Lec.	0.20	135	1.00	4.00	-	fair	73.3	37.0	11.4	14.2	770
Lec.	0.20	135	1.00	4.00	-	fair-good	65.8	62.8	10.6	12.5	745
Lec.	0.20	135	1.05	4.00	Batch was well mixed but not castable - scrapped.						
Lec.	0.20	135	1.05	4.00	-	good	95.2	92.7	10.4	11.5	1102
Lec.	0.20	135	1.05	4.25	-	good	83.3	77.9	11.4	13.4	877
Lec.	0.20	135	1.05	4.25	-	good	91.7	84.5	11.3	13.8	1019
Lec.	0.20	135	1.05	4.25	-	fair	89.6	86.1	10.3	11.7	1013
Lec.	0.20	135	1.05	4.25	-	good	95.6	95.4	10.6	11.3	1086
C-1	0.10	135	1.05	4.25	-	fair	191.7	191.5	12.6	13.0	1988
rosol TR	0.20	135	1.05	4.25	-	Batch had begun to set-up in the mixer.					
rosol TR	0.20	135	1.05	4.25	-	good	55.3	50.8	12.4	15.0	527
C-1	0.10	135	1.05	4.25	-	good	138.5	138.1	11.5	12.5	1592
C-1	0.10	135	1.05	4.25	-	good	Used to obtain safety data.				
C-1	0.10	135	1.05	4.25	-	good	Used to obtain safety data and 4-1 lb motors for a ballistic determination of specific impulse.				
C-1	0.10	135	1.05	4.25	-	good	169.4	163.8	14.5	16.0	1498
							Used to obtain burning rate data.				
C-1	0.10	135	1.05	4.25	-	good	Used to obtain a complete failure envelope and constant strain data.				

Table XXXVIII Footnotes

[a]All propellants based on Telagen S (Lot 148AH), HDI, CTI, and IDP (25% of binder).

[b]Blend 13 consists of 35.8, 32.10, and 32.10 wt% of oxidizers of average particle size 6, 148, and 419μ, respectively. Standard Blend 13 consists of the same amounts of the unscreened oxidizers from which the above indicated monoblend systems were derived.

[c]Valley Metallurgical Company, spherical.

(U) Three particle sizes of spherical aluminum were used in different propellants in order to determine the effects on mixing, casting and mechanical properties. There was little difference in mechanical properties, as shown in Table XXXVIII, but the smallest particle size (8-14 micron) used in Propellant 20 gave poorer mixing and casting. The largest particle size (40-50 micron) used in Propellant 19 was more satisfactory, althoug there was little noticeable difference from the 30-40 micron size used in Propellant 18.

(U) Since only a small percentage of the standard as received grinds of oxidizer was screened out to make up the monoblend systems, standard grinds without previous screening were used in the same percentages as were used to prepare Blend No. 13. (Compare Propellants 22 and 25 where 25 contained the standard grinds.) The blend with the unscreened oxidizers was called Standard Blend No. 13.

(U) Relatively good mixing and casting were obtained using lecithin as a wetting agent, but generally the mechanical properties of these propellants were poor. Aerosol TR was used as a wetting agent in an effort to obtain better mechanical properties but showed little advantage over lecithin. In the case of batches which were one pound or larger, and which contained C-1, mixing was good and the best mechanical properties were obtained.

(U) Based on the accumulated data, the formulation used in Propellant 25 was selected as the candidate propellant. Propellants 25-29 had identical formulations except that the oxidizer in Batch 28 was dried under vacuum at 140°F in the presence of molecular sieve pellets. This batch gave better mixing and casting and somewhat better mechanical properties showing that even trace amounts of moisture on the oxidizer has a marked effect on the propellant.

k. High Solids Propellant-Composition and Theoretical Performance (U)

(U) The composition of the high solids propellant and its theoretical performance are shown in Table IXL.

Table IXL*

COMPOSITION AND THEORETICAL PERFORMANCE OF HIGH SOLIDS PROPELLANT (U)

(C)

Component	Wt. %
NH_4ClO_4	79.00
Aluminum	12.00
Telagen S	6.41
CTI	0.096
HDI	0.490
IDP	2.00
C-1	0.10
FeAA	0.004
HAA	0.006

*Table IXL cont on next page.

Table IXL (Cont)

Specific Impulse, lbf-sec/lbm	Wt. %
Theory[a]	261.7
Expected[b]	248.0
Effective[b] (k = 0.7) (Second Stage Minuteman Wing VI - 246.1)	249.4

[a]1000 psia exhausting to atmospheric pressure and 0° half angle.
[b]1000 psia exhausting to atmospheric pressure and 15° half angle.

1. Safety Studies (U)

(U) Safety data obtained from Batches 26 and 27 are given in Table XL.

Table XL

SAFETY DATA FOR HIGH SOLIDS LOADED PROPELLANT (U)

Bureau of Mines impact - 50% Point, cm/2kg	12.8
Autoignition Temperature, °F	570
DTA - Endothermic Peak, °F	474
Exothermic Peaks, °F	600
Ignition, °F	645
Thermal Stability - 200°F/64 hr	No change
Wood Blocks - #8 blasting cap only	Negative, burned 29 sec
#8 blasting cap with 5-gm booster	Negative, (5 each)
NOL Card Gap - Zero attenuation	Negative, (2 each)

m. Mechanical Behavior (U)

(U) A 60-lb batch of 91% solids propellant was made and tested mechanically at from -75 to 150°F and from 1.6×10^{-4} to 80 in./in./min strain rate.

Table XLI

MECHANICAL BEHAVIOR OF HIGH SOLIDS LOADED (91%) PROPELLANT (U)

Test Temp °F	Mechanical Properties[a] ($\sigma_{nm}/\epsilon_m/\epsilon_b/E_o$) at Strain Rate, in./in./min				
	0.00016	0.008	0.8	8.0	80
-75	953/4/4/31500	1107/2/2/69600	1328/2/2/99700	781/0.5/0.5/167000	1500/1/1/11600
-40	578/4/4/15100	635/3/3/28200	860/3/3/50000	948/2.0/2.0/85000	1130/3/3/65800
0	370/8/8/5820	366/6/6/8300	586/6/6/6000	738/4/4/27900	755/6/6/25200
20	271/8/9/3430	218/8/10/3430	358/8/10/7260	503/8/13/13200	689/7.1/10/16600
77	74/10/11/758[b]	94/10/12/1060	155/11/13/2110	206/9/11.0/2820	353/11/16/6040
150	25/9/10/327[b]	40/11/15/478	87/10/13/1100	122/10/11/638	170/12/16/20

[a] End-bonded specimen ; 2.5 in. gauge length. See Table XLII for comparison with Instron specimen.

[b] Strain rate 0.0002 in./in./min.

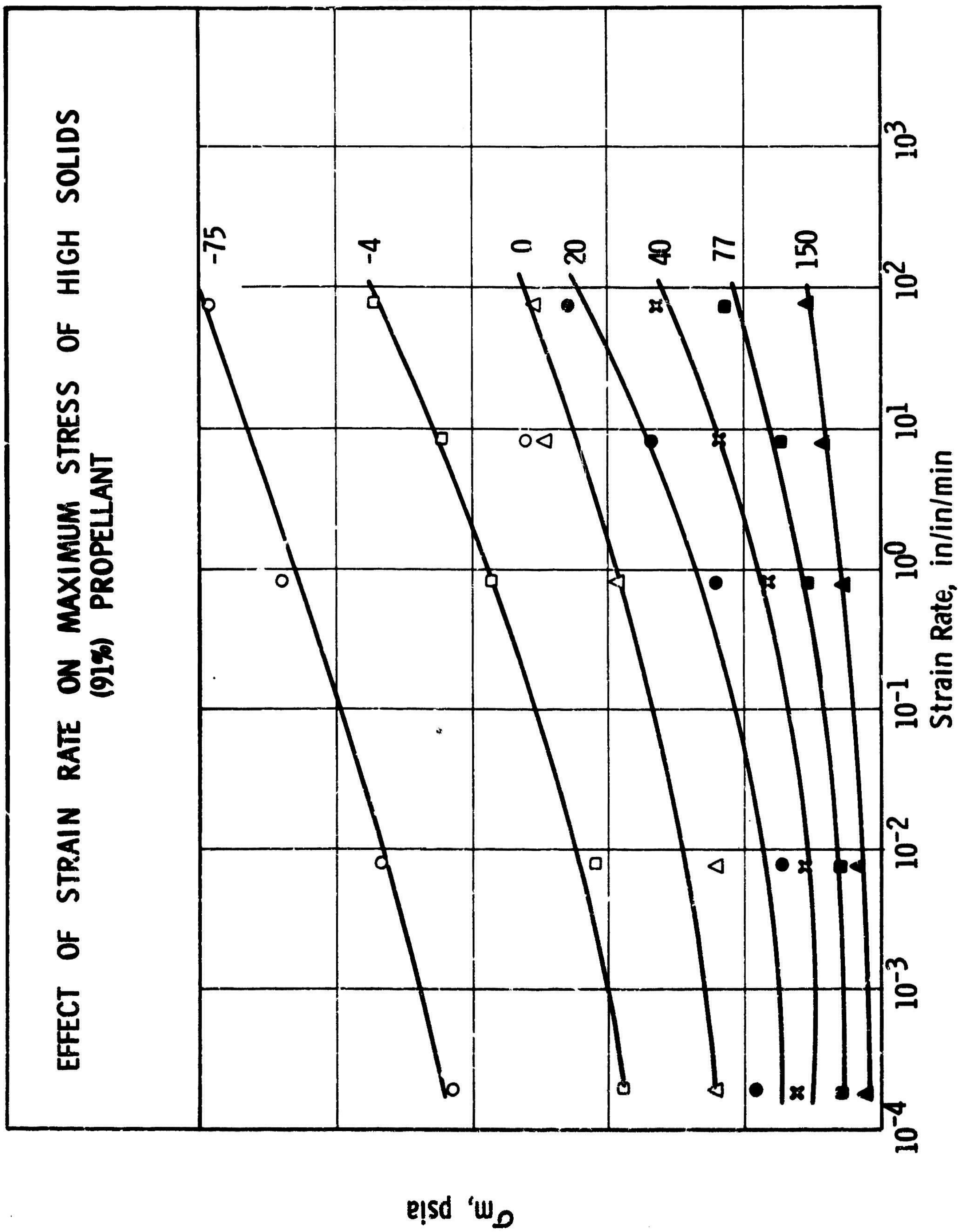
Table XLII

MECHANICAL BEHAVIOR OF HIGH SOLIDS LOADED (91%) PROPELLANT (U)

Test Temp °F	Mechanical Properties[a] ($\sigma_m/\epsilon_m/\epsilon_b/E_o$) at Strain Rate, in./in./min				
	0.000148	0.0074	0.74	7.4	74.0
-75	499/2/3/27100	1093/2/2/69000	1299/2/2/100000	798/0.9/0.9/92600	1300/1/1/125000
-40	638/5/6/5000	695/4/4/22500	920/3/3/44000	929/2/2/54600	1110/3/3/46500
0	363/7/7/5630	377/6/7/7100	564/9/9/10800	742/6/7/17900	750/7/7/20600
20	286/8/8/3530	218/11/11/2580	350/13/16/4380	492/11/13/7640	674/8/10/13000
40	156/8/10/1790	155/15/15/1340	248/15/16/2450	327/15/20/3270	506/12/16/7170
77	78/13/14/683[b]	89/15/16/730	151/14/16/1430	197/17/19/1850	348/14/21/4570
150	29/13/13/285[b]	42/13/15/410	75/15/20/600	113/14/16/420	152/16/20/1730

[a] Standard Instron specimen; 2.7 in. gauge length. See Table XLI for comparison with end-bonded specimen.

[b] Strain rate 0.000185 in./in./min.



EFFECT OF STRAIN RATE ON MAXIMUM STRESS OF HIGH SOLIDS (91%) PROPELLANT

Figure 49

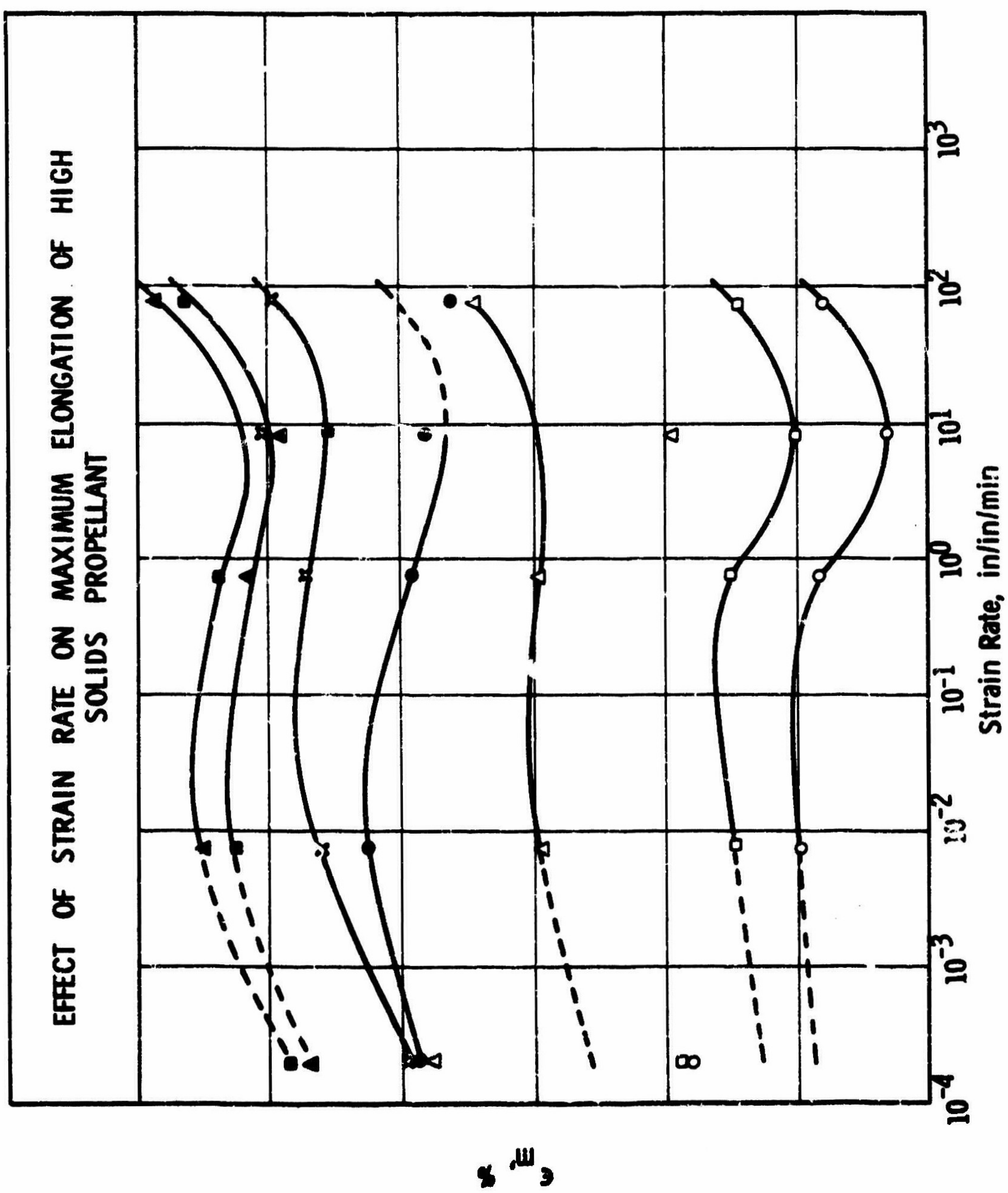

EFFECT OF STRAIN RATE ON MAXIMUM ELONGATION OF HIGH SOLIDS PROPELLANT
ϵ_m, %
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
Strain Rate, in/in/min

Figure 50

(U) The data are reported in Tables XLI and XLII. Table XLI gives data for end-bonded specimens of 2.5-in. gauge length and Table XLII, data for standard Instron specimens of 2.7-in. gauge length. Figures 49 and 50 show the variation of maximum stress and elongation as a function of strain rate. The elongation data of Figure 50 showed inconsistency and scatter at very low strain rate so the curves drawn to these data points were approximate. There was also an inconsistency in the data points at strain rates at 8.0 and 80 in./in./min. Either all the elongations at 8 in./in./min were too low or those at 80 in./in./min were too high. These inconsistencies did not occur in the stress data (Figure 49).

(U) The data of Table XLI were used to derive a failure envelope for the propellant. Figure 51 shows all the maximum stress data shifted to correct for temperature and strain rate. The abscissa represents the time to reach maximum strain ($t_s = \epsilon_s$/strain rate). Figure 52 shows the variation of the shift factor a_T with temperature and comparison with the WLF equation $\log a_T = 8.86\ (T-T_s)/(10.16 + T-T_s)$ gives $T_s = 278°K$ (40°C). If $T_s = T_g + 50$, the glass transition temperature of the propellant would be -10°C.[g] Figures 53 and 54 are the propellant failure envelopes.

(U) At 40°F and 30% relative humidity all test samples held 7.5% strain (75% of maximum) for one week and 50% held 10% strain.

n. Burning Rate Studies (U)

(U) Burning rate data on the candidate propellant were obtained from a series of 10-gram (0.75C-0-1.5) Rohm and Haas micromotors. These data are reported in Table XLIII and Figure 55.

Table XLIII

MICROMOTOR BURNING CONDITIONS[a] (U)

Burning Surface Area to Nozzle Throat Area Ratio	Chamber Pressure, avg. psia	Web Burning Pressure, Avg. psia	Burning Rate in./sec
155	351	383	0.325
174	672	822	0.587
197	992	1231	0.81
216	1368	1395	0.95

[a]Data plotted in Figure 55.

(U) The burning rate pressure exponent was 0.78. This exponent is relatively high, but it should be noted that an exponent of 0.70 was obtained for a propellant with 88 wt% solids. No attempts were made to modify either the rate or the pressure exponent.

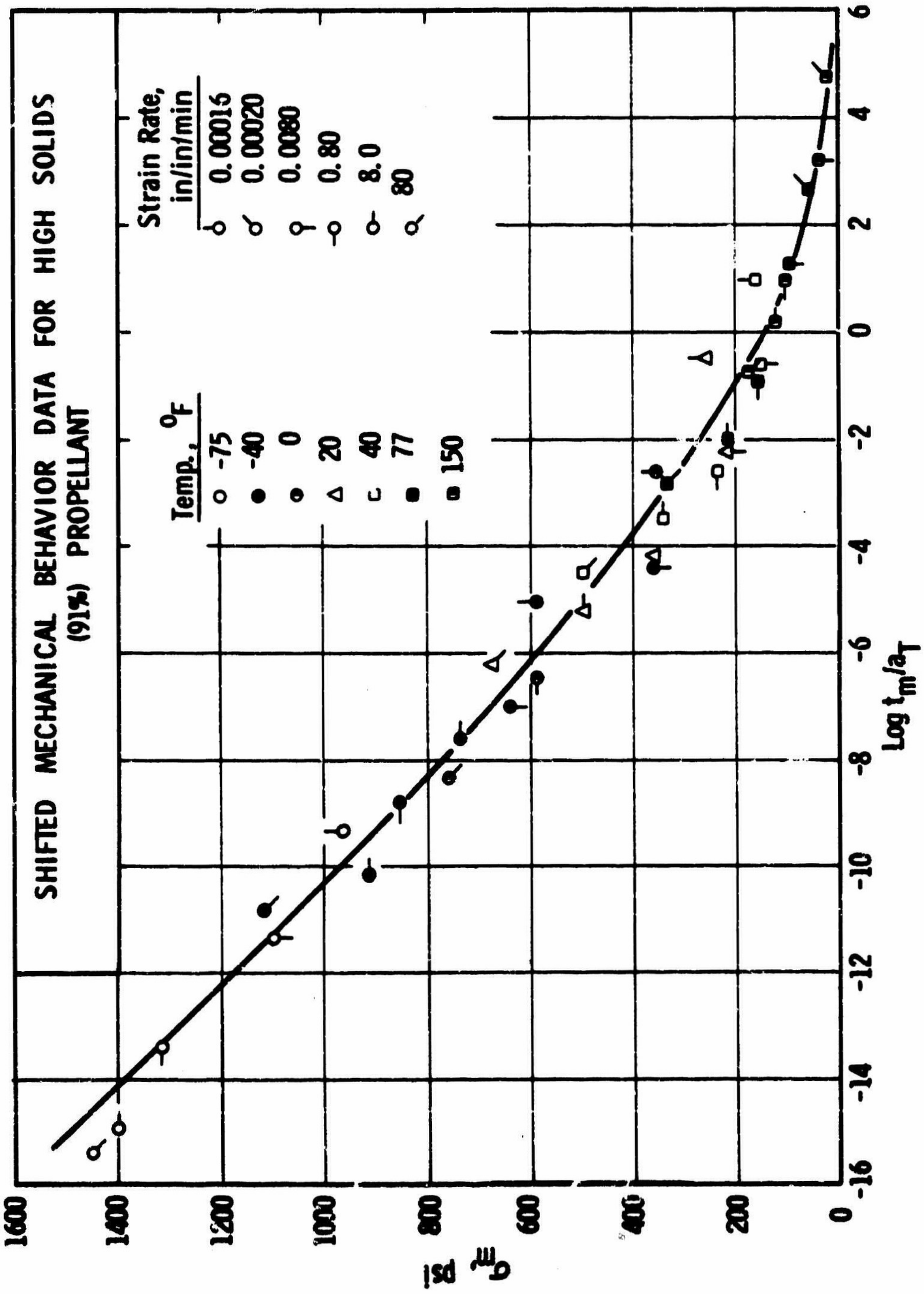

SHIFTED MECHANICAL BEHAVIOR DATA FOR HIGH SOLIDS
(91%) PROPELLANT
Temp., °F
-75
-40
0
20
40
77
150
Strain Rate, in/in/min
0.00015
0.00020
0.0080
0.80
8.0
80
σ_m, psi
0
200
400
600
800
1000
1200
1400
1600
Log t_m/a_T
-16
-14
-12
-10
-8
-6
-4
-2
0
2
4
6

Figure 51

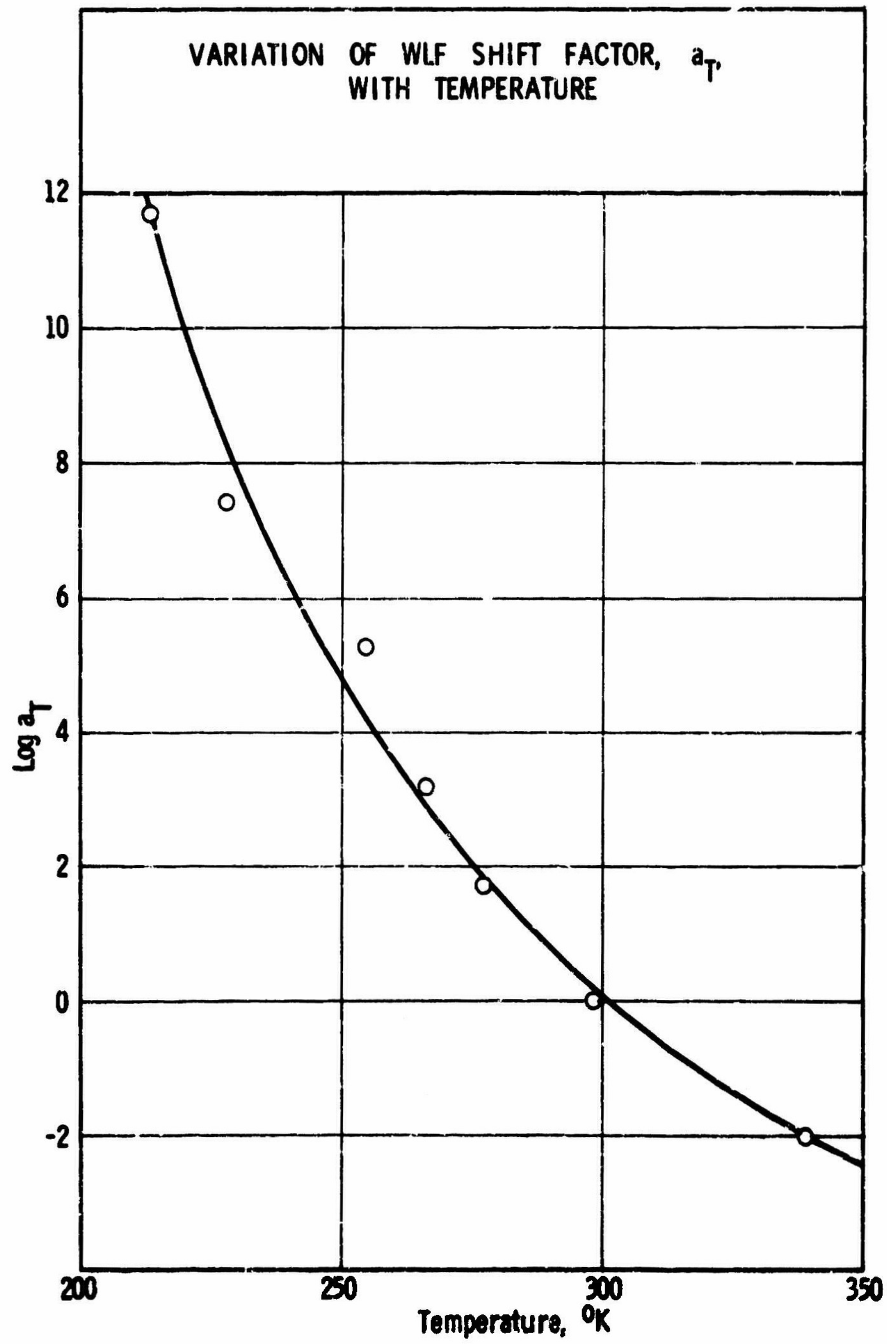

VARIATION OF WLF SHIFT FACTOR, a_T, WITH TEMPERATURE
12
10
8
6
4
2
0
-2
Log a_T
200
250
300
350
Temperature, °K

Figure 52

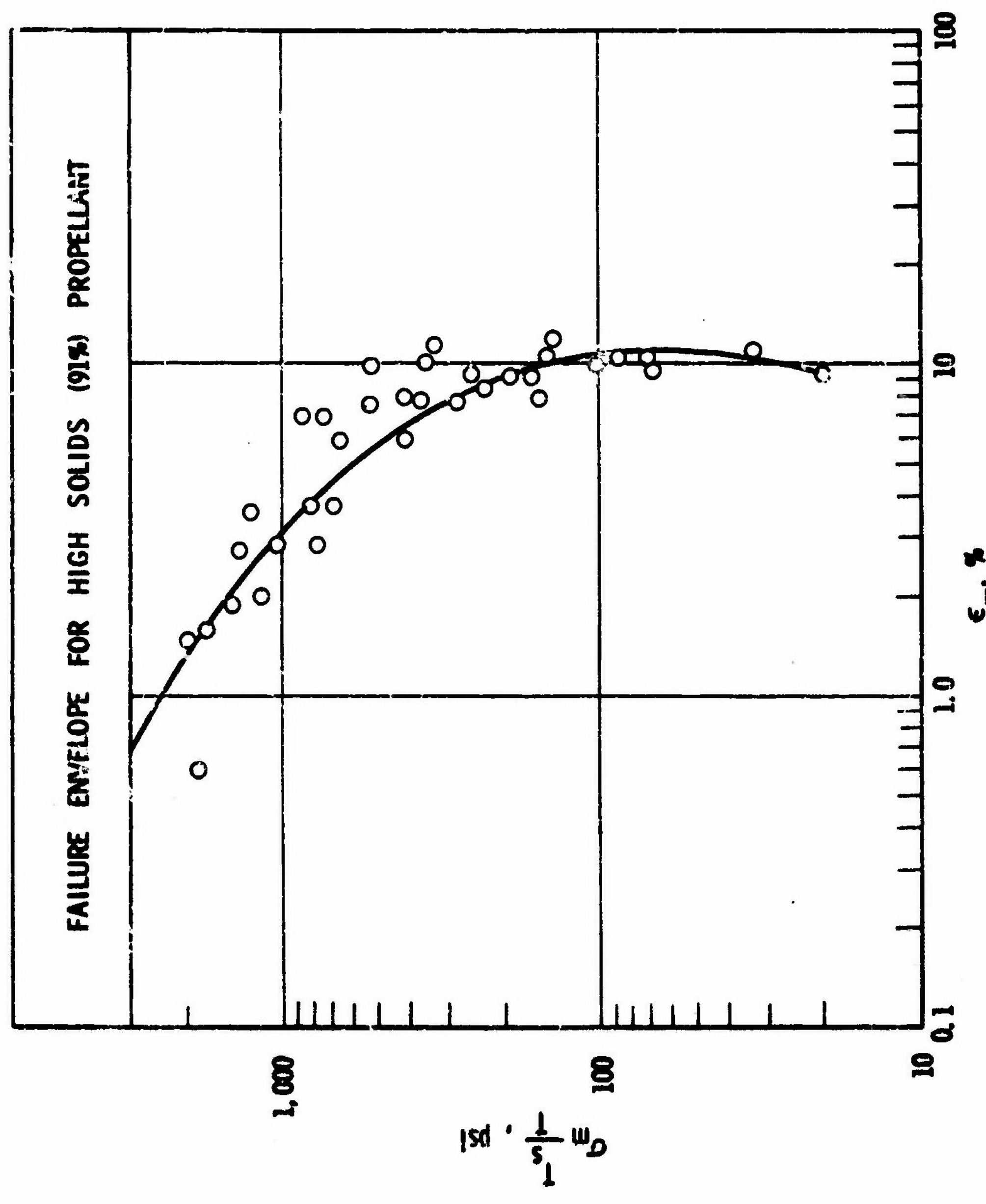

FAILURE ENVELOPE FOR HIGH SOLIDS (91%) PROPELLANT
0.1
1.0
10
100
ϵ_m, %
10
100
1,000
$\sigma_m \frac{T}{T_s}$, psi

Figure 53

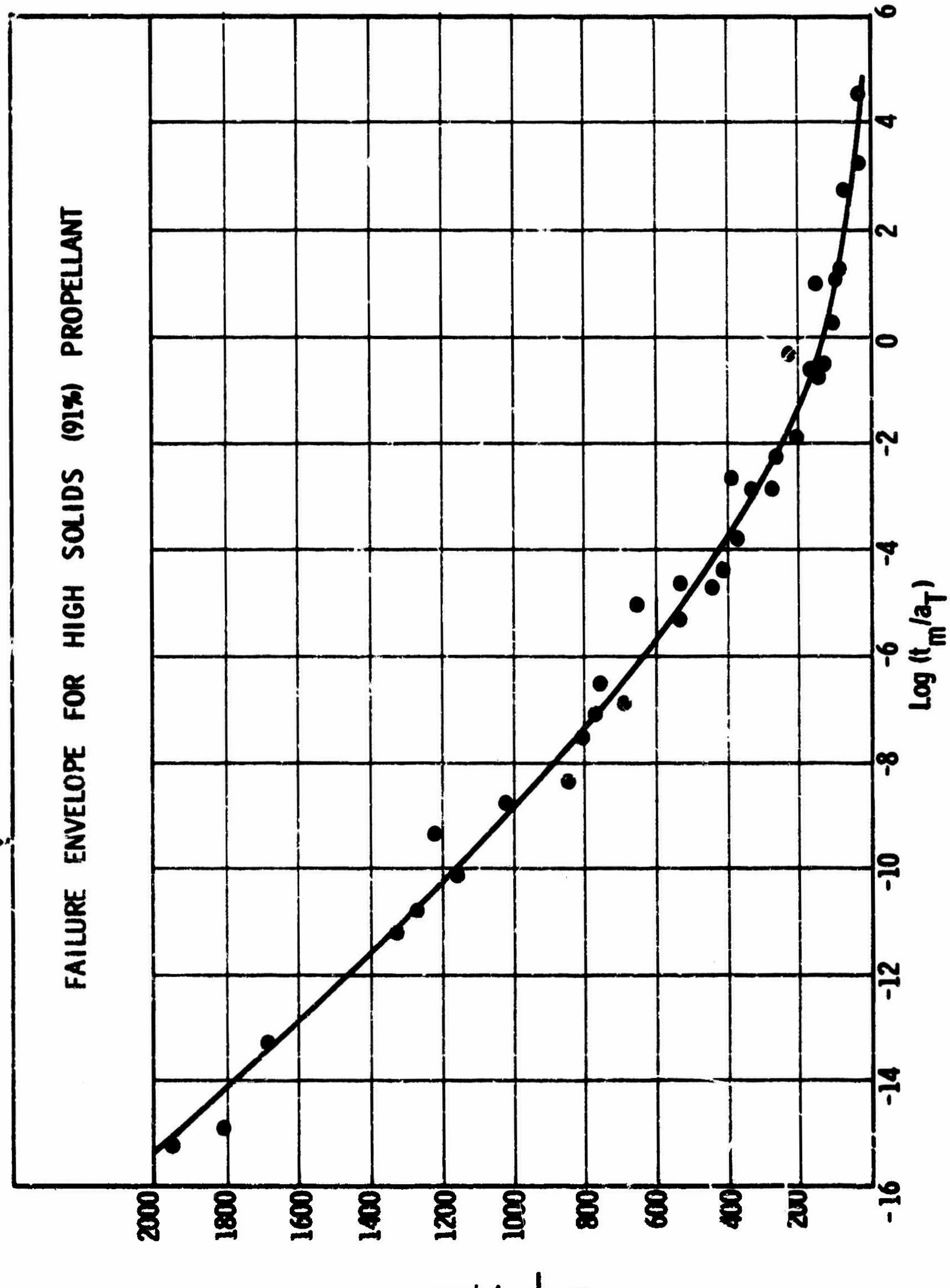

FAILURE ENVELOPE FOR HIGH SOLIDS (91%) PROPELLANT
2000
1800
1600
1400
1200
1000
800
600
400
200
-16
-14
-12
-10
-8
-6
-4
-2
0
2
4
6
Log (t_m/a_T)
$\sigma_m \frac{1}{S_1}$, psia

Figure 54

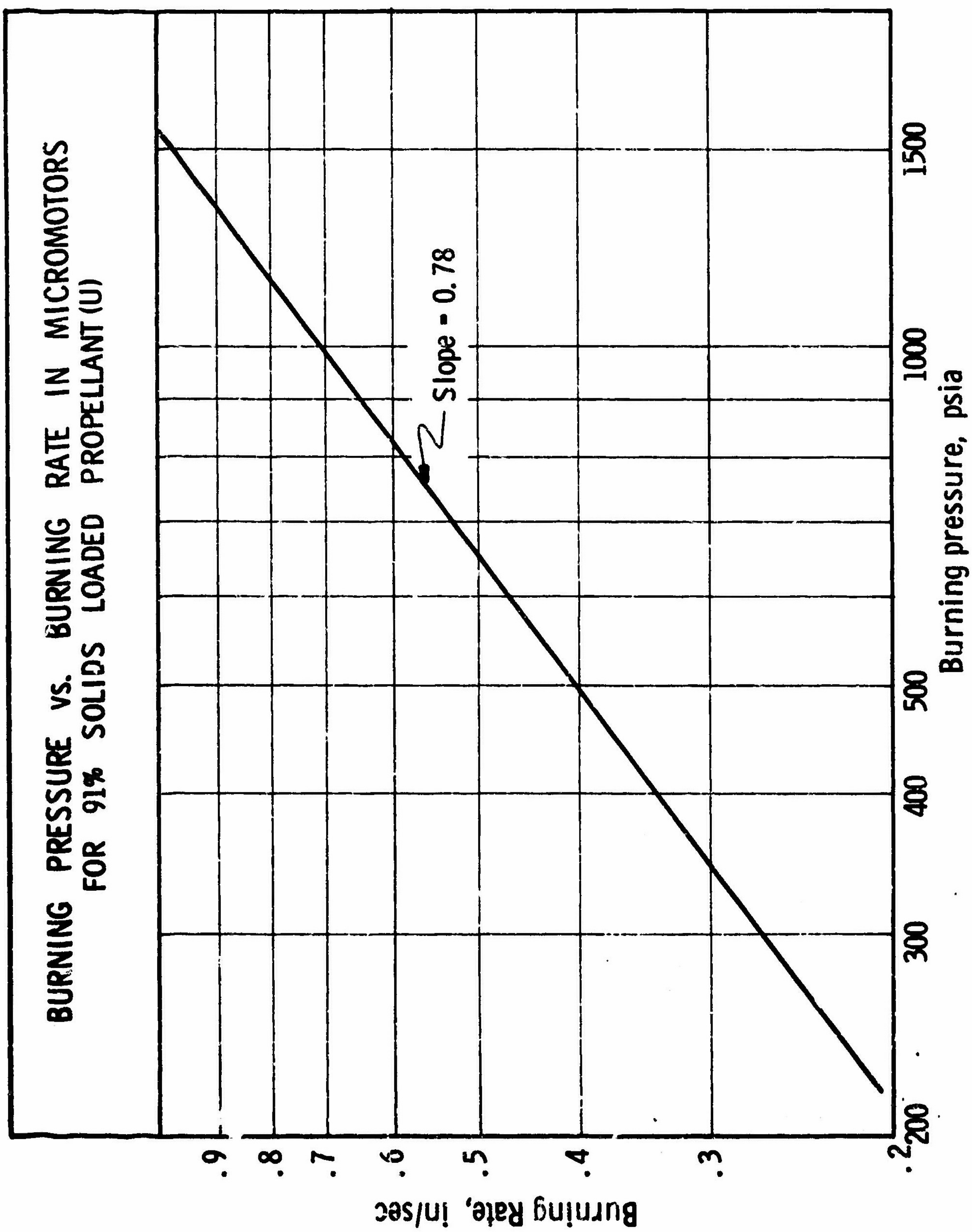


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Figure 55

o. Ballistic Performance (U)

(U) Four 1-lb motors containing the high solids propellant were fired to determine the expected performance of the propellant. Of the motors tested two gave both a thrust and pressure trace, one gave only a thrust trace, and one overpressured and gave no data. The data obtained from the firings which gave both a pressure and thrust trace are summarized in Table XLIV and the pressure and thrust traces are shown in Figures 56 and 57.

Table XLIV

BALLISTIC PERFORMANCE[a] OF HIGH SOLIDS (91%) PROPELLANT (U)

	Motor	
	1	2
Average Chamber Pressure, psia	628	993
Measured Specific Impulse, lbf-sec/lbm	227	239.8
Standard Specific Impulse,[b] lbf-sec/lbm	241	240.0
(C) Expected Large Motor Specific Impulse,[c] lbf-sec/lbm	249	248
Expected Specific Impulse Density Performance,[d] lbf-sec/lbm	251	250

[a]1KS-250 size motors.
[b]1000 psia exhausting to 14.7 psia, 15° half-angle.
[c]By use of scaling factor derived for conventional NH_4ClO_4-Al propellants.

$$^{d}I_s = I_s^{15}\left(\frac{1.82}{1.80}\right)^{0.7}$$

(C) The scale-up data indicate that the specific impulse expected in large motors will be very close to the calculated 248 lbf-sec/lbm. The data for effective specific impulse (I_{s0}) indicate that this propellant would outperform the current Minuteman Wing VI Second Stage Propellant by at least 4 impulse units in a lower stage.

(U) The first motor fired experienced ignition difficulties which were solved by abrading the grain surface and by using an aluminum frangible disk on the nozzle to allow the chamber pressure to rise to about 500-600 psia. The remaining motors were fired in this manner.

PRESSURE-THRUST TRACE FOR 1 KS-250 SIZE MOTOR WITH HIGH SOLIDS (91%) PROPELLANT (U)

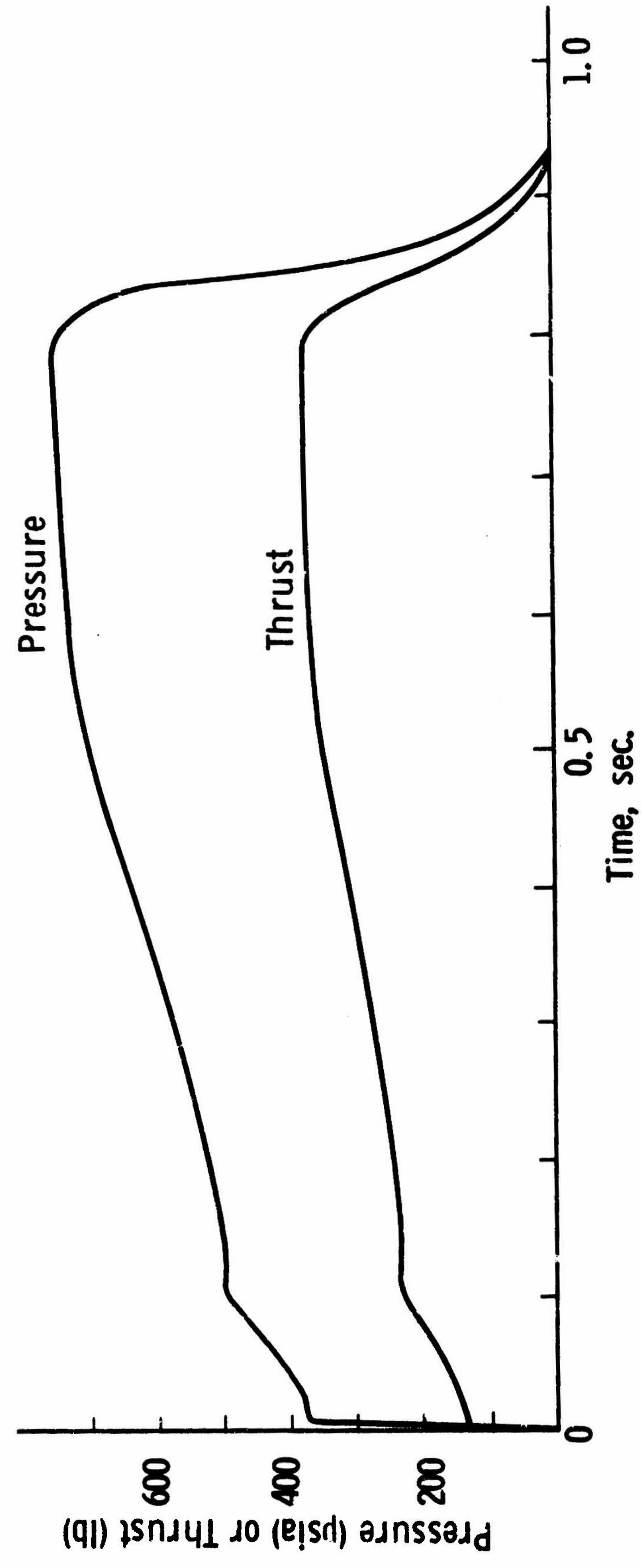


Figure 56

PRESSURE-THRUST TRACE FOR 1KS-250 SIZE MOTOR WITH HIGH SOLIDS (91%) PROPELLANT (U)

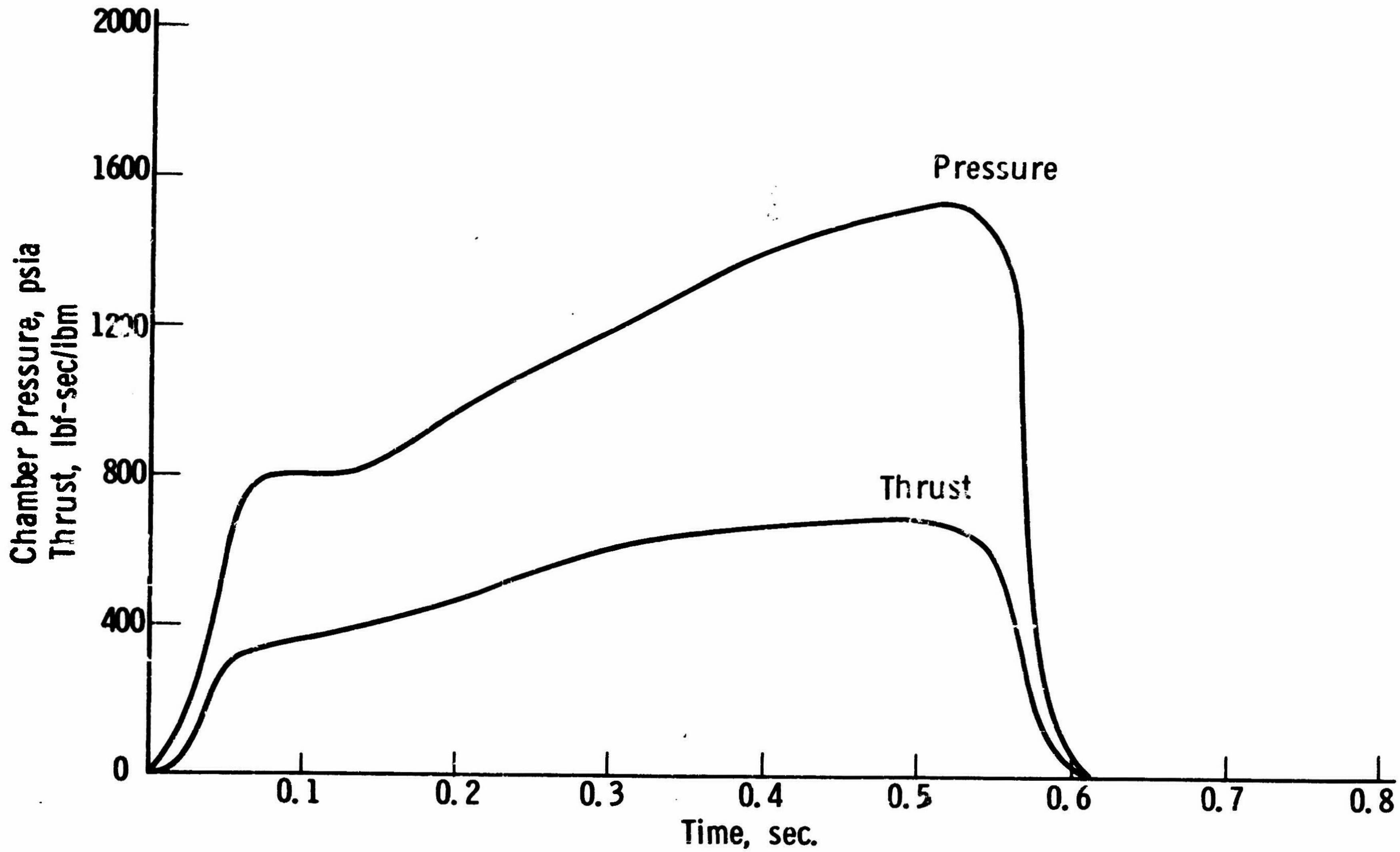


Figure 57

p. High Solids Propellant-Recommendations (U)

(U) This approach to high solids propellants and this propellant is recommended to the Rocket Propulsion Laboratories for careful consideration. The following points concerning this propellant should be considered.

(U) 1) This propellant is a prototype. Although the mechanical properties will probably never be better than those of less highly loaded propellant, nevertheless, they can be improved and may be useful for a wide range of applications.

(C) 2) This propellant is not the most energetic which could be formulated, although it is at least 4 units better in impulse-density than the current Minuteman Wing VI Second Stage Propellant. Replacement of some oxidizer with fuel will give higher delivered impulse and higher density with improved processability.

(U) 3) The total solids loading could be increased to 92%. Until very recently, this goal seemed unattainable, but new work by Farris[13] which allows the calculation of the viscosity of multimodal suspensions from available unimodal viscosity data make higher solids loadings possible.

(U) 4) This approach to higher impulse is desirable because only conventional ballistic materials are used. These materials are inexpensive and readily available.

9. Prepolymer Specifications (U)

(U) Tentative specifications for secondary-hydroxy-terminated, saturated polybutadiene were drawn up and are shown in Table XLIVa. Further changes will be made and the question of a specification for functionality may require much further consideration. Below are some considerations concerning the specifications.

a. Molecular Weight (U)

(U) The molecular weight of the prepolymer should not be less than 1500. The upper limit is a function of the viscosity specification, but will generally lie near 2000. Thus, the upper limit should be the highest molecular weight consistent with the maximum allowable viscosity (see below).

b. Equivalent Weight (U)

(U) The equivalent weight is not a basic specification, but rather a derived one. It is determined by the limits placed on two more important properties, molecular weight and functionality.

c. Functionality (U)

(U) The functionality which may be the single most important variable is difficult to measure. The functionality defined as the ratio of

molecular weight to equivalent weight is not adequate per se since prepolymers with molecular weight to equivalent weight ratios of less than 1.5 have been satisfactorily cured with a trifunctional reagent.

Table XLIVa

TENTATIVE SPECIFICATIONS FOR SATURATED PREPOLYMER (U)

Molecular Weight	1800 ± 300
Hydroxyl Content, meq/gm	0.75 - 1.33
Maximum Unsaturation, mm/gm	1.0
Pendant Ethyl Content, %[a]	35 ± 10
Viscosity, poises at 25°C	150 - 300
Maximum Ash, %	0.03
Maximum Moisture, %	0.025
Maximum Volatiles, %	1.0
Maximum Iron Content, ppm	50

Functionality, when cured with isocyanate, Mobay E-246, resulting gumstock should equal or exceed in value at least 2 of the following three parameters and not be off by more than 3% on the third.

Hardness, Shore 00	85
Williams Plasticity	230
Gel fraction, %	82

[a]Pendent ethyl is expressed as the percent 1,2-addition during polymerization of the butadiene.

(U) More appropriate at this time is a specification based upon a measured property of the cured prepolymer. The Shore 00 hardness, Williams Plasticity and gel fraction are suggested as properties which may be measured. In addition, Aerojet recommends the procedure of making at least three binders of differing crosslink densities and all containing the prepolymer and cured with combinations of CTI and HDI. The extent of cure and functionality of the binders would be determined by solvent swelling, by compression moduli of the swollen samples, and by Mooney-Rivlin constants at 77°F. This is not a rapid method, but no rapid method can be recommended at this time.

(U) It is likely that more data from a current Air Force sponsored program to develop a method of determining functionality will become available to guide this phase of the specifications.

d. Unsaturation (U)

(U) The maximum degree of saturation consistent with the other specification variables is desirable. The maximum unsaturation should be 1.00 millimole per gram of prepolymer. This value will be satisfactory for conventional propellants, but a lower value might be required for some advanced propellants.

e. Pendent Ethyl Content (U)

(U) The pendent ethyl content of the prepolymer shall be specified on the basis of the 1,2-addition occurring during polymerization of the butadiene and shall be measured on the prepolymer before hydrogenation. A method of determining this parameter on the saturated prepolymer remains to be developed. There has been no indication that this variable affects the polymer properties in a major fashion. An increase of pendent groups will increase the viscosity of the prepolymer and, in this manner, affect the molecular weight (see molecular weight specification). The pendent ethyl content should be restricted to the range 25 to 45%.

(U) For a hydrogenated prepolymer the amounts of cis- and trans-1,4-addition in the unsaturated prepolymer will presumably have little effect since hydrogenation destroys the possibility of geometric isomerism. Therefore, no specification shall be made for the amount of cis- and trans-1,4-addition in the unsaturated prepolymer.

f. Brookfield Viscosity (U)

(U) The viscosities of hydroxy-terminated Telagen S have been in the range 160-200 poises at 25°C with the molecular weight of about 1800. The original specification corresponded roughly to that found useful for the prepolymer used for the Minuteman Wing VI Second Stage prepolymer and this specification is continued. Therefore, the Brookfield viscosity shall not exceed 300 poises at 25°C. The current product is well below this upper limit and it seems wise at this time to designate a lower limit of 150 poises at 25°C in order that the molecular weight of the prepolymer be kept as high as is consistent with propellant processing requirements. It is possible that higher molecular weight prepolymers will improve the low temperature mechanical properties of the Telagen S propellants and that this lower limit may have to be revised upward.

g. Ash (U)

(U) The ash content may represent residue of a metallic nature which would be derived from corrosion products, hydrogenation catalyst and alkyl metal polymerization catalysts. The ash content shall be limited to less than 0.03%.

h. Iron Content (U)

(U) Iron, the most common metal contaminant with possible harmful effects shall not exceed a total of 50 ppm.

i. Antioxidant (U)

(U) The antioxidant levels of the Telagen S prepolymers used thus far have been very low or nil. No specification will be set at this time, but this will be subject to change as required.

C. PHASE II (U)

1. Introduction (U)

(U) Phase II involved preliminary study of the compatibility of the candidate prepolymer, curing agents, or suitable models with advanced oxidizers and fuels. Materials which were compatible were tested in propellants.

2. Use of Model Systems (U)

(U) The use of model compounds to study the chemical interaction between binder components and oxidizers or fuels has proved to be a powerful tool. The model compound allows the chemist to carry out analyses which are difficult or impossible to achieve with the prepolymers and curing agents used to prepare propellants. The result is that not only are incompatibilities uncovered, but information concerning the nature of the incompatibility is also obtained.

(U) The model compound or compounds should be low molecular weight replicas of some structural or chemical characteristic of the prepolymer or curing agent. It is not always necessary that a single model show all the characteristics of its counterpart. In some cases it is expedient and convenient to use several models each showing only one characteristic of the material of interest. This approach has been used in this program where three model compounds are used to describe the chemical behavior of Telagen S.

(U) A useful characteristic of the model compound is its volatility so that analysis by gas-liquid chromatograph (GLC) is possible. GLC is a very useful method for discovering and studying unexpected chemical interactions. All the models used in this program have this property.

3. Model Compounds (U)

(U) Three compounds were used as models for the hydroxy-terminated Telagen S. These were 2-octanol (J. T. Baker Chemical Co., 90% pure by GLC), 1-decanol (Eastman Kodak Co., white label, pure by GLC), and 1,7-octadiene (Columbian Carbon Company, used as received). The first two compounds represent the primary and secondary hydroxy groups of the potential prepolymer while the olefin is characteristic of the residual unsaturation. In a similar fashion the carboxy terminated Telagen S was represented by 1-nonanoic acid (Emery Industries Inc., redistilled, b.p. 129°C/5 mm; pure by GLC), 2-ethylhexanoic acid (Union Carbide Corp., pure by GLC and used as received) and 1,7-octadiene.

(U) Phenyl isocyanate (Eastman Kodak Co., white label; redistilled b.p. 166°C; pure by GLC) was used as a model isocyanate and the solvents,

n-hexane (Fisher Scientific Co., spectroanalyzed grade) and toluene (J. T. Baker, Reagent grade; distilled from sodium) were used to represent the hydrocarbon portions of Telagen S. Bibenzyl, toluene and phenylcyclohexane were used as internal markers for the GLC studies.

(U) In addition to these models n-butyl isocyanate (Eastman Kodak Co., practical grade, redistilled, b.p. 111-112°C) a model isocyanate, 1-benzoyl-2-ethylaziridine, a model aziridine, 1,2-epoxycyclohexane (Research Organic Chemicals Co., C.P.) a model epoxide and propionic (J. T. Baker Chemical Company, reagent grade) and hexanoic (Matheson, Coleman, and Bell, practical grade) acids, model carboxylic acids, were used in the continued studies of the effects of advanced fuels and oxidizers on binder ingredients. The aziridine was prepared by the reaction of benzoyl chloride with 2-ethylaziridine and distilled, b.p. 82-85°C at 0.2 mm. Crotyl alcohol (J. T. Baker Chemical Co., b.p. 122-123, impure by GLC) was used for special studies described in the text.

4. Method for Studying Compatibility of Advanced Ingredients with Model Compounds (U)

(U) The samples were prepared in a tared 1 dram shell vial within a weighing bottle. The tared bottle and vial were put into a dry nitrogen atmospheric box where the ingredient sample was put into the shell vial. The weighing bottle was sealed, removed from the dry box in order to weigh the ingredient and then returned to the dry box. The shell vial was fitted with a rubber serum cap after introduction of 0.5 ml of a solution containing a model compound, and removed from the box for gas chromatographic analysis. Chromatograms for some of the model compounds are shown in Figures 58 to 61. Stored or heated, samples were sealed into 2-ml ampules prepared essentially by the method described above. The gas chromatographic analyses were performed on an F & M Model 500 Gas Chromatograph equipped with a katharometer detector. A sample size of 10μl was used for each analysis. Table XLV shows the column conditions used for the separations.

5. Advanced Fuels (U)

a. Hydroxy Compounds (U)

(U) The alcohols, 2-octanol and 1-decanol were compatible with LMH-1, and chrome passivated Be at 50°C for 18 hours (Table XLVI) and only small losses of alcohol were observed after 34 days.

b. Olefinic Compounds (U)

(U) The unsaturated compound, 1,7-octadiene, showed a slight decrease in concentration, about 5%, after 34 hours at 50°C in the presence of the same fuels (Table XLVII). No new compounds were detected by gas chromatography and no gas evolution was observed. Olefins were concluded to be compatible with the advanced fuels.

GAS-LIQUID CHROMATOGRAM OF A TOLUENE SOLUTION OF BIBENZYL, 2-OCTANOL, AND 1-DECANOL

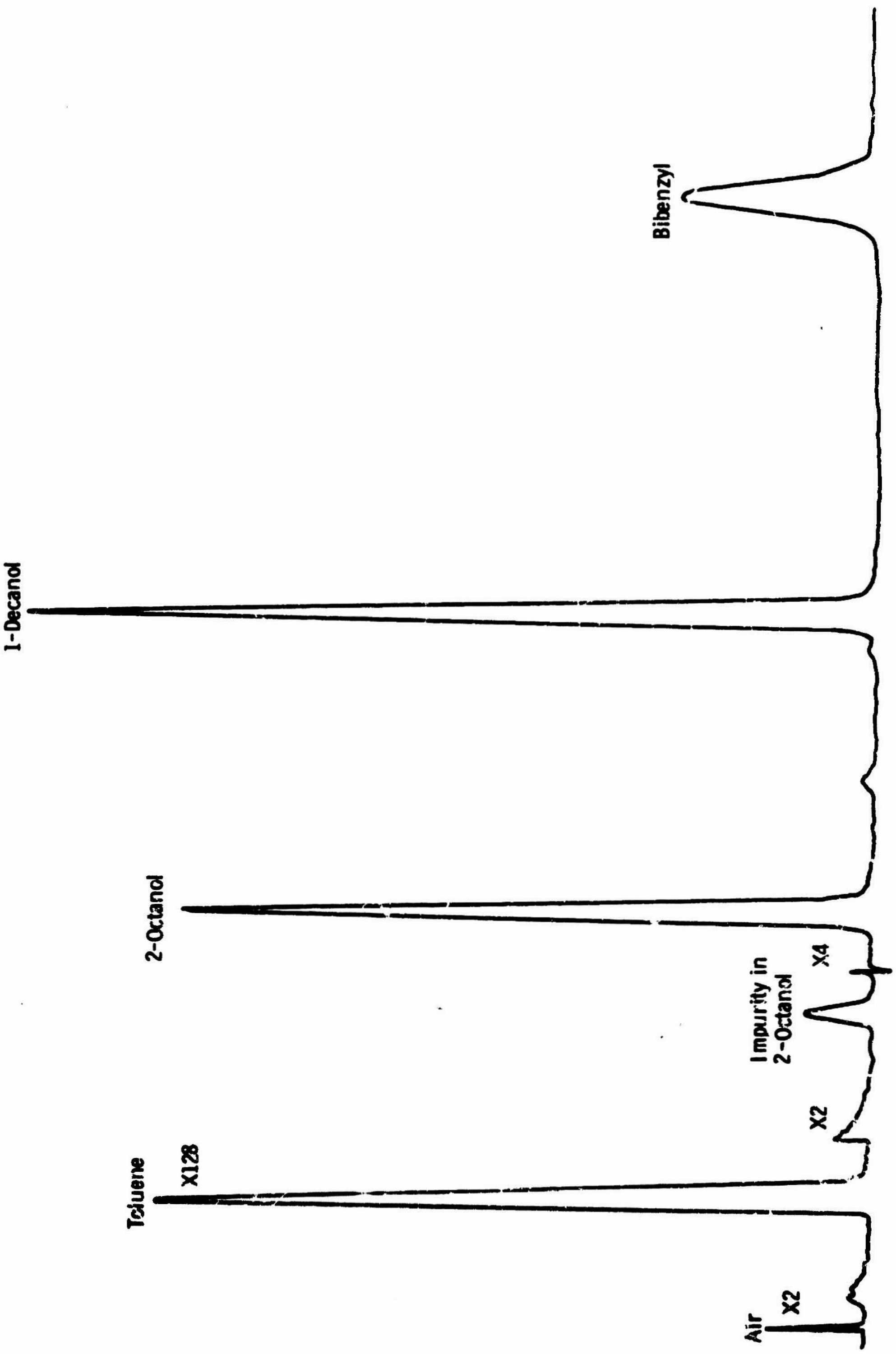


Figure 58

GAS-LIQUID CHROMATOGRAM OF A HEXANE SOLUTION OF TOLUENE AND 1,7-OCTADIENE

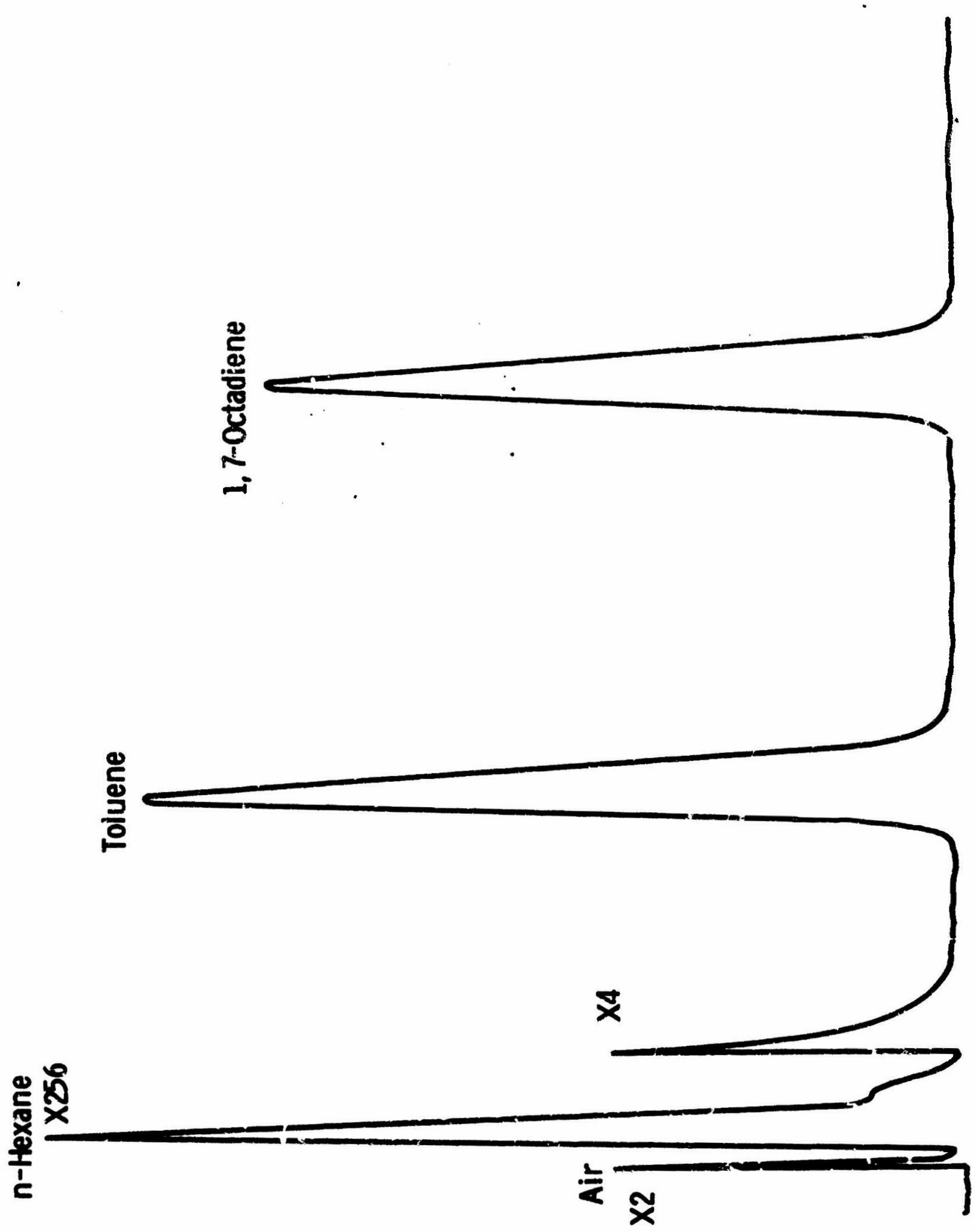


Figure 59

GAS-LIQUID CHROMATOGRAM OF A TOLUENE SOLUTION OF PHENYLCYCLOHEXANE, 2-ETHYHEXANOIC ACID AND NONANOIC ACID KEPT OVER CHROME PASSIVATED Be FOR 18 HOURS AT AMBIENT TEMPERATURE

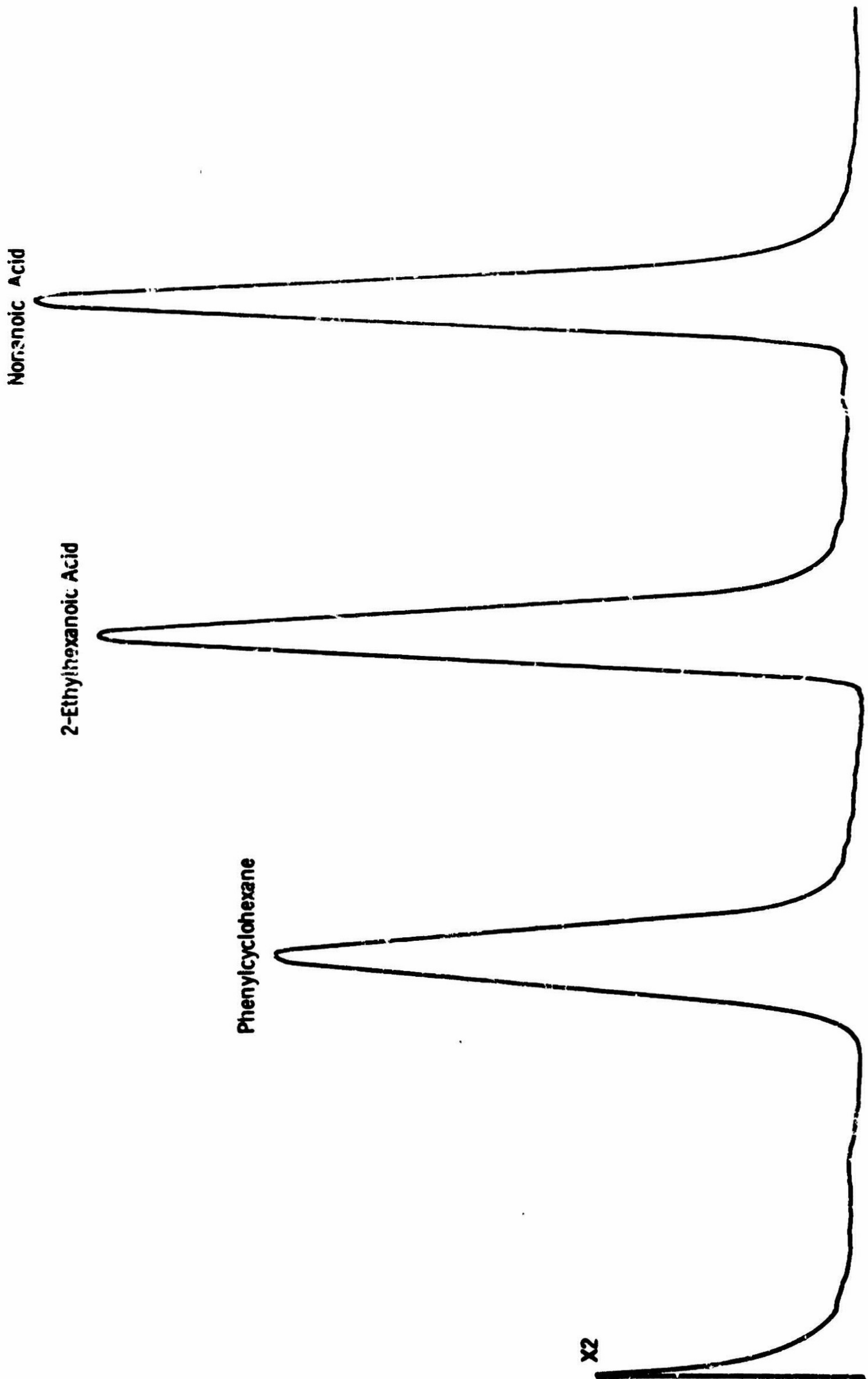


Figure 60

GAS-LIQUID CHROMATOGRAM OF A TOLUENE SOLUTION OF PHENYL ISOCYANATE AND PHENYLCYCLOHEXANE

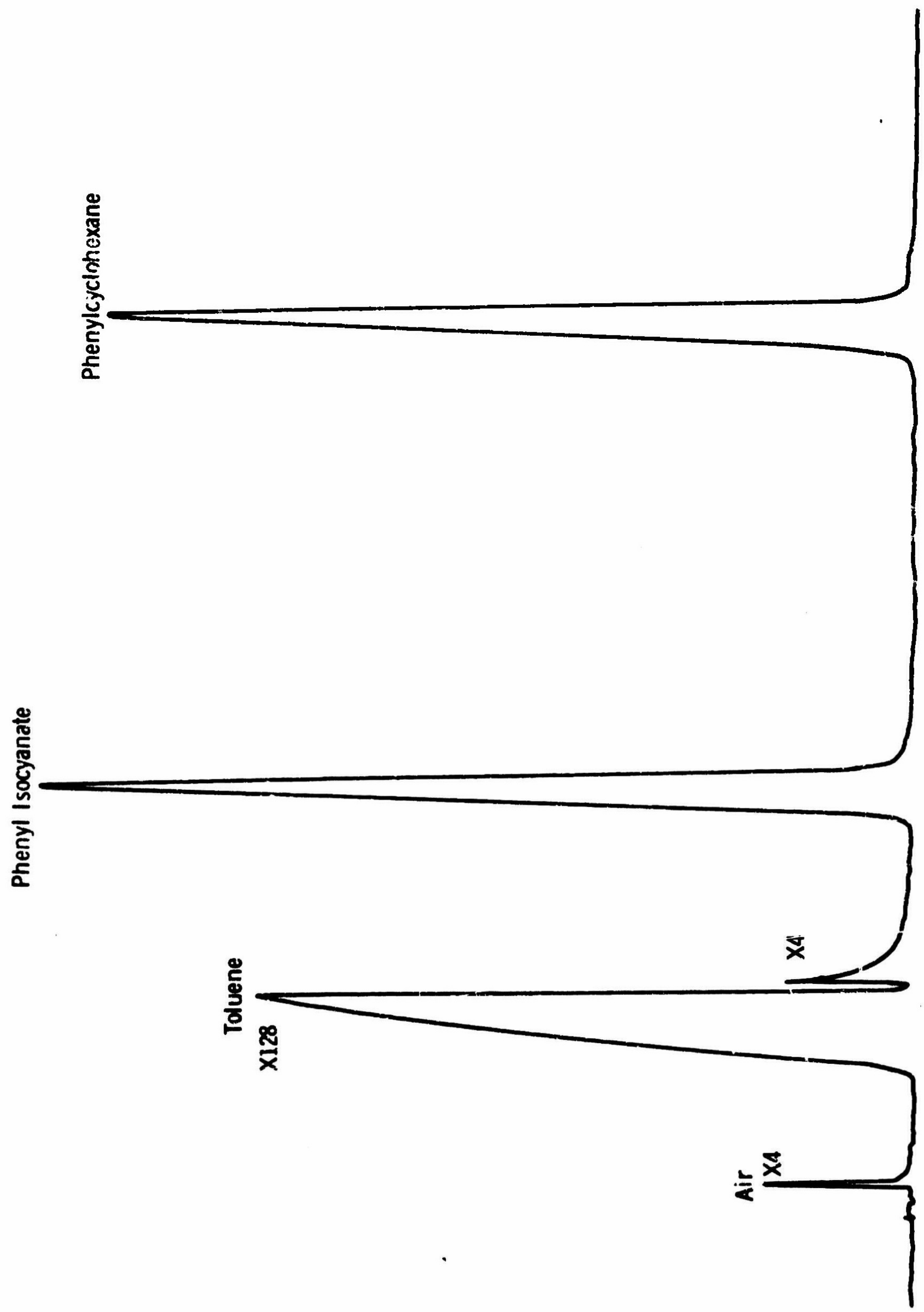


Figure 61

Table XLV

CHROMATOGRAPHIC CONDITIONS FOR ANALYSES OF MODEL SYSTEMS BY GLC (U)

	Alcohols	Olefins	Acids	Isocyanates	Alcohol-Isocyanate	Aziridine-Acid	Epoxide-Acid
Column Material	1[a]	1[a]	2[b]	3[c]	4[d]	5[e]	1[a]
Temperature, °C	100-200	50-75	100-150	55-134	75-225	115	100-225[f]
Heating Rate, °C/min	15	21	7.9	15	21	0	-
Gas Flow, ml/min	100	100	20	60	100	100	60
Injection Port Temp., °C	200	190	200	200	200	175	200
Block Temp., °C	300	300	300	300	300	300	300
Bridge Current, m.a.	150	150	150	150	150	150	150

[a] 4' x 1/4" stainless steel; 10% Carbowax 20M on 60-80 mesh Diatoport S.
[b] 2' x 1/4" stainless steel; 10% ethylene glycol succinate on 60-80 mesh Diatoport S.
[c] 2' x 1/4" stainless steel; 10% silicone gum rubber SE-30 on 60-80 mesh Diatoport S.
[d] 2' x 1/4" stainless steel; 20% DC 705 on 80-100 mesh Diatoport S.
[e] 1½' x 1/4" stainless steel; 5% Carbowax 6000 on 80-100 mesh Diatoport S.
[f] Stepwise heating: 100°C/10 min; 225°C to end.

Table XLVI

COMPATIBILITY[a] OF 2-OCTANOL AND 1-DECANOL WITH ADVANCED FUELS (U)

Time, hr	Temp °C	LMH-1: ROH^d	LMH-1: $C_8H_{17}OH$	LMH-1: $C_{10}H_{21}OH$	Be: ROH^d	Be: $C_8H_{17}OH$	Be: $C_{10}H_{21}OH$	LMH-2: ROH^d	LMH-2: $C_8H_{17}OH$	LMH-2: $C_{10}H_{21}OH$
0	-	4.6	100	100	3.5	100	100	-	-	-
18	23	4.6	100	99	3.5	100	100	-	-	-
18	23	2.2	100[b]	100[b]	-	-	-	-	-	-
18	50	6.5	100	100	5.1	99	100	-	-	-
18	50	2.7	100[c]	101[c]	-	-	-	-	-	-
18	23	2.2	100[b]	100[b]	-	-	-	-	-	-
816	50	2.0	100	100	2.0	94	92	2.0	99	99

[a] % of original alcohol remaining; bibenzyl used as internal standard.

[b] LMH-1 treated; ground in ball mill, exposed to ambient air for 48 hrs, dried 20 hrs at 60°C and 0.1 mm pressure.

[c] Freshly ground LMH-1.

[d] Weight ratio.

Table XLVII

COMPATIBILITY[a] OF 1,7-OCTADIENE WITH ADVANCED FUELS (U)

		LMH-1		Be	
Time, hr	Temp, °C	LMH-1: Olefin[c]	% Olefin	Be: Olefin[c]	% Olefin
0	-	8.8	100	18.5	100
18	23	8.8	99	18.5	100
18	23	2.2	100[b]	-	-
18	50	8.7	96	18.9	98
816	50	8.0	95	8.0	98

[a] % of original 1,7-octadiene remaining; toluene used as internal standard.
[b] LMH-1 treated (footnote b, Table XLVI)
[c] Weight ratio.

c. Carboxy Compounds (U)

(U) The carboxylic acids, nonanoic acid and 2-ethylhexanoic acid, exhibited some reactivity with LMH-1, but not with the passivated Be (Table XLVIII) after 18 hours. The branched carboxylic acid, 2-ethylhexanoic acid, was stable even after 18 hr at 50°C on freshly ground LMH-1, whereas the nonanoic acid showed a 3% decrease in concentration on the unground LMH-1 and a 10% change on the freshly ground LMH-1 under the same reaction conditions. Considerable loss of both acids occurred after 34 days at 50°C with both LMH-1 and Be. Gaseous evolution was observed, especially with the ground LMH-1, but no new products were detected by gas chromatography. It is concluded from these observations that neutralization of the acid was occurring.

(U) It was concluded that the carboxy functional group was compatible with advanced fuels with some reservations. These reservations did not apply to LMH-2, but for compatibility the LMH-1 should be pretreated and the Be, chrome-coated.

d. Isocyanate Compounds (U)

(U) The hydroxy-terminated Telagen S is cured with isocyanates. The compatibility of phenyl isocyanate, the model compound for the curing agents, with the advanced fuels is summarized in Table XLIX. The isocyanate was reactive in the presence of fuels showing a decrease of 9% on LMH-1 and 26% on chrome-coated Be after 18 hours at 50°C. Gas evolution was noted in the case of LMH-1, but no new products were observed for either case by the gas chromatography.

Table XLVIII

COMPATIBILITY[a] OF NONANOIC AND 2-ETHYLHEXANOIC ACIDS WITH ADVANCED FUELS (U)

Time, hr	Temp, °C	LMH-1: LMH-1: Acid[d]	LMH-1: $C_8H_{17}COOH$	LMH-1: $C_7H_{15}COOH$	Be: Be: Acid[d]	Be: $C_8H_{17}COOH$	Be: $C_7H_{15}COOH$	LMH-2: LMH-2: Acid[d]	LMH-2: $C_8H_{17}COOH$	LMH-2: $C_7H_{15}COOH$
0	-	3.5	100	100	4.4	100	100	-	-	-
18	23	3.5	100	100	4.4	99	100	-	-	-
18	23	2.2	95[b]	100[b]	-	-	-	-	-	-
18	50	4.4	97	100	4.5	100	104	-	-	-
18	50	3.8[c]	90[c]	98[c]	-	-	-	-	-	-
18	50	2.2	87[b]	100[b]	-	-	-	-	-	-
816	50	2.0	44	58	2.0	52	66	-	100	100

[a] % of original acid remaining; phenylcyclohexane used as an internal standard.
[b] LMH-1 treated (footnote b, Table XLVI).
[c] Freshly ground LMH-1.
[d] Weight ratio.

Table XLIX

COMPATIBILITY[a] OF PHENYL ISOCYANATE WITH ADVANCED FUELS (U)

Time, hr	Temp, °C	LMH-1		Be	
		LMH-1: C_6H_5NCO[b]	C_6H_5NCO	Be: C_6H_5NCO[b]	C_6H_5NCO
0	-	11.0	100	12.5	100
48	23	9.3	91	10.0	80
18	50	12.0	91	15.0	74

[a] % of original C_6H_5NCO remaining; phenylcyclohexane used as an internal standard.
[b] Weight ratio.

(U) Butyl isocyanate was similarly reactive with the advanced fuels, including pretreated LMH-1 (Table L). The order of loss of isocyanate was LMH-2 > Be > LMH-1. The type of isocyanate, aromatic or alkyl, made little difference in stability with the fuels (Table LI).

Table L

COMPATIBILITY[a] OF n-BUTYL ISOCYANATE WITH ADVANCED FUELS (U)
(18 hours)

Fuel	Fuel/Component Weight Ratio	Temp, °C 23	Temp, °C 50
LMH-1	12	95	88
LMH-1[b]	2.2	88	74
Be	13	77	69
LMH-2	9	-	60

[a] % of original C_4H_9NCO remaining.
[b] LMH-1 treated (footnote b, Table XLVI).

Table LI

COMPATIBILITY[a] OF ISOCYANATES WITH ADVANCED FUELS (U)
(18 hours at 50°C)

Fuel	C_6H_5NCO	n-C_4H_9NCO
LMH-1	91	88
Be	74	69
LMH-2	-	60

[a]% of original isocyanate remaining.

(U) Because the workhorse binder is isocyanate-cured, a more thorough investigation of the interaction of isocyanates with LMH-1 was made. The LMH-1 was chosen because studies indicated that it presented greater problems of compatibility than did the other fuels.

(U) Samples of HDI in two evacuated, sealed tubes with treated (footnote b, Table XLVI) and untreated LMH-1 at 50°C for 24 hr produced gas. The gas analyzed by mass-spectrometry had the composition indicated below (Table LII).

Table LII

MASS SPECTROMETRIC COMPOSITION (mol %) OF GASES PRODUCED BY HDI IN THE PRESENCE OF LMH-1 (U)

LMH-1	H_2	H_2O	N_2	O_2	Ar	CO_2
Untreated	17.57	0.43	3.54	1.63	0.17	76.66
Treated	8.87	0.60	1.15	0.28	0.11	88.99

The analysis indicated no CO. Possibly the isocyanate was reacting with water adsorbed on the oxide coating of the LMH-1 to give CO_2. This has support in the fact that twice as much gas was formed with the treated LMH-1 where the treatment requires grinding to smaller particle size and then exposing to moisture to form an oxide coating.

(U) Pretreated LMH-1 was reacted with a benzene solution of n-butyl isocyanate at 50°C for 5 days. The LMH-1 was filtered from the solution, washed with benzene and dried under vacuum. The major product in the solution besides the n-butyl isocyanate reactant, was N,N'-dibutylurea. (I.R. analysis) The formation of the urea is in accord with the CO_2 production

observed from the mass spectral analysis of the gases produced from the reaction of HDI with LMH-1. The formation of a substantial amount of urea and CO_2 can be postulated to occur through the reaction of the isocyanate with moisture or some other -OH function adsorbed on the surface of LMH-1 to form carbamic acid. The carbamic acid is thermally decomposed to CO_2 and an alkyl amine which reacts with excess isocyanate to form a urea.

(U) The LMH-1 filtered from the benzene solution was added to a fresh solution of n-butyl isocyanate and heated at 50°C for 20 hours. A chromatographic analysis of the reaction solution showed the loss of 55% of the isocyanate.

(U) It is apparent that pretreating the LMH-1 with isocyanate will not completely eliminate its reactivity with the isocyanate.

e. Isocyanate-Alcohol Reaction Systems (U)

(U) A model isocyanate curing system was studied in the presence of advanced fuels. A comparison with a control experiment of the reaction between 1-butyl isocyanate and 2-octanol indicated that the presence of beryllium or LMH-2 had no effect on the rate of formation or the amount of the urethane product (Table LIII). There was an initial loss of 6 and 12%, respectively, of isocyanate when beryllium or LMH-2 was present, suggesting that the isocyanate was reacting with water on the surface of the untreated fuels. The isocyanates were not completely unreactive in the presence of advanced fuels (Tables L and LI). Losses of isocyanate up to 40% were observed in the presence of the untreated advanced fuel when no alcohol was present. This greater loss of isocyanate was ascribed to homopolymerization of the isocyanate and the reaction of isocyanate with water to form carbamic acid. The subsequent thermal decomposition of the carbamic acid could produce an amine, which would react further with the isocyanate to form a urea derivative, and carbon dioxide. The latter possibility was substantiated as indicated in the previous paragraphs for LMH-1, and by the data in Table LIV.

(U) The amount of isocyanate lost to side reaction of isocyanate with water was small but comparison with dried samples of chrome passivated Be and LMH-2 showed a complete reduction of this loss of isocyanate on Be and a 50% reduction of the loss on LMH-2 (Table LIV).

(U) This essentially solved the compatibility problem for Be and LMH-2 with isocyanate. As indicated, however, pretreatment of the LMH-1 did not improve its compatibility with isocyanates. The approach to compatibility was made by reducing the cure temperature for isocyanates with appropriate catalysts. The catalyst T-12 (Metal & Thermite Corp; dibutyltin dilaurate) and T-20 (Metal & Thermite Corp; sulfur-tin organic of unknown structure) afforded complete reaction overnight at room temperature. A small loss of isocyanate to side reactions was evidenced by the formation of less than the theoretical amount of urethane (Table LV and LVI).

Table LIII

RATE OF REACTION OF n-BUTYL ISOCYANATE AND 2-OCTANOL IN CONTACT WITH ADVANCED FUELS AT 50°C[a] (U)

Control (no additives)

Time, hr	R-NCO %	R-OH %	Prod %	Σ(R-OH+Prod) %
0	100	100	0	100
4	84	86	10	96
8	74	74	21	95
18	51	55	37	92
24	42	44	48	93
48	19	21	72	93

Be[b]

Time, hr	R-NCO %	R-OH %	Prod %	Σ(R-OH+Prod) %
4	80	86	15	101
8	65	70	21	91
18	48	57	36	93
24	36	37	47	84
48	16	23	67	90

LMH-2[b]

Time, hr	R-NCO %	R-OH %	Prod %	Σ(R-OH+Prod) %
8	70	81	21	102
18	38	51	43	94
24	27	37	50	87
44	10	23	69	92

[a]NCO to OH = 1:1 equivalent ratio.

[b]Fuel to component weight ratio is 2.2:1.

Table LIV

THE EFFECT OF DRYING[a] Be AND LMH-2 ON COMPATIBILITY WITH n-BUTYL ISOCYANATE AND 2-OCTANOL AT 50°C (U)

Time, hr	Fuel	RNCO Remaining %	Deviation from Control
4	Control	49.0	-
	Be	48.4	0.6
	LMH-2	45.3	3.7
	Be (dried)	49.3	-0.3
	LMH-2 (dried)	47.4	1.6

[a] Be and LMH-2 dried over P_2O_5 at 80°C and 1mm vacuum for 72 hours.

Table LV

CATALYZED REACTION OF n-BUTYL ISOCYANATE WITH 2-OCTANOL AT 23°C IN BENZENE[a] (U)

Catalyst	Composition, %				
	Time, min	C_4H_9NCO[b]	$C_8H_{17}OH$[b]	Urethane[c]	Total Alcohol + Urethane
T-12	30	68.5	62.4	32.5	94.9
	60	58.8	47.2	48.0	95.2
	90	43.9	33.0	56.5	89.5
	1440	23.0	6.0	83.8	89.8
T-20	30	76.0	72.3	23.2	95.5
	60	65.0	56.6	36.8	93.4
	90	54.4	42.6	46.3	89.4
	1440	24.6	6.8	83.0	89.8

[a] 0.1% catalyst based on total weight.
[b] Percent of original.
[c] Percent of urethane theoretically possible from the initial alcohol (Note: C_4H_9NCO was in 39% excess).

Table LVI

CATALYZED REACTION OF n-BUTYL ISOCYANATE WITH 2-OCTANOL IN THE PRESENCE OF LMH-1 (TREATED) AT 23° and 50°C IN BENZENE[a] (U)

Temp	Catalyst	Composition, % Time, min	C_4H_9NCO[b]	$C_8H_{17}OH$[b]	Urethane[c]	Total Alcohol + Urethane
23°C	T-12	30	73.1	58.8	33.7	92.5
		90	52.6	43.3	47.8	91.1
		1440	2.9	0	86.5	86.5
	T-20	30	73.2	82.8	16.1	98.9
		60	62.5	61.6	33.8	95.4
		90	52.0	46.5	45.7	92.2
		1440	2.9	0	87.5	87.5
	none	1440	66.1	85.6	11.2	96.8
50°C	none	1440	23.4	50.4	36.9	86.9
	T-12	1440	0	0	85.5	85.5
	T-20	1440	0	0	87.0	87.0

[a]Binder to LMH-1 wt. ratio 4:1 and 0.1% catalyst based on total weight.
[b]Percent of original.
[c]Percent of urethane theoretically possible from the initial alcohol (Note: C_4H_9NCO was in 3[illegible]% excess).

(U) The catalysts T-12 and T-20 were pretreated with HAP and NH_4ClO_4 to determine the effect, if any, on their catalytic activity (Table LVII). The catalytic activity of T-20 was greatly reduced when pretreated with HAP. Treatment involved 15 minute contact of benzene solution of the catalyst with the oxidizers.

Table LVII

REACTION OF n-BUTYL ISOCYANATE WITH 2-OCTANOL AND PRETREATED CATALYSTS AT 23°C FOR 15 MINUTES IN BENZENE[a] (U)

		Composition, %			
Catalyst	Treatment[a]	C_4H_9NCO[b]	$C_8H_{17}OH$[b]	Urethane[c]	Total Alcohol + Urethane
T-12	none	80.4	79.4	17.4	96.8
T-12	NH_4ClO_4	79.6	77.6	21.5	99.1
T-12	HAP	79.5	77.4	20.0	97.4
T-20	none	76.8	78.0	19.2	97.2
T-20	NH_4ClO_4	73.3	79.4	19.4	98.8
T-20	HAP	93.5	96.0	3.2	99.2

[a] 0.1% catalyst based on binder weight; catalyst solutions pre-contacted with HAP or NH_4ClO_4 for 15 minutes.
[b] Percent of original.
[c] Percent of urethane theoretically possible from the initial alcohol (Note: C_4H_9NCO was in 39% excess).

(U) Systems based on the use of catalysts T-12 and T-20 allowed LMH-1-NH_4ClO_4 propellants to be prepared and cured.

f. Workhorse Binder and Propellant Ingredients (U)

(U) Along with the model compound studies, investigations with actual propellant ingredients were made as a check on the model studies.

(U) Hydroxy terminated Telagen S showed no adverse effects in the presence of chrome coated Be, LMH-1 or LMH-2, i.e., no gassing or viscosity increase.

(U) Binders were prepared using CTI, hexamethylene diisocyanate and hydroxy terminated Telagen S (0.32:0.71:1.0 eq) with an equal weight

of Be and LMH-1. In the case of LMH-2 a 2:1 weight ratio of binder to LMH-2 was used because of mixing difficulties. After six days at 50°C, the binders with Be and LMH-2 were hardening but the sample with LMH-1 was gassing. These results were consistent with the model studies and pointed to incompatibility of the isocyanate group with LMH-1.

(U) A mixture of hydroxyl terminated Telagen S and untreated LMH-1 showed gas bubbles when kept at 135°F for four days. No bubbles or other reactions were observed in mixtures of the prepolymer with chrome coated Be or of the prepolymer and untreated LMH-2 after 20 days at 135°F. Similar results were obtained in mixtures of the isocyanates and advanced fuels. A mixture of HDI, CTI and LMH-1 showed gas bubbles when stored at 135°F for 14 days. Similar mixtures using chrome coated Be and LMH-2 gave no evidence of gas evolution under the same conditions.

(U) Binder samples containing LMH-1 gave evidence of foaming during a 135°F cure. Samples with chrome coated Be and LMH-2 did not foam and cured within 5 days at 135°F. Impact sensitivities of the above samples were greater than 100 cm/2 kg weight, the limit of the apparatus used.

(U) The actual binder ingredients were tested for compatibility with LMH-1 by measuring gas evolution and only the isocyanates, HDI and CTI, were found to be incompatible. Table LVIII gives the changes in gas evolution with time for the various binder ingredients.

Table LVIII

GAS EVOLUTION[a] FROM THE LMH-1 WITH VARIOUS BINDER INGREDIENTS AT 54°C (U)

Time, days	Control[b] mm	Prepolymer mm	HDI mm	IDP mm	CTI mm
1	0.5	1.3	14.2	0.25	7.0
2	1.0	2.0	16.3	0.45	7.9
6	2.7	4.0	28.4	0.97	14.1
8	3.7	5.3	37.1	1.47	17.8

[a]Relative change in manometer height, millimeters
[b]LMH-1 only.

(U) Binders with IDP and the advanced fuels were prepared. After six days at 50°C, the binder with LMH-1 was gassing. The others were curing normally; the binder with LMH-2 being twice as hard as the binder with Be.

(U) Tests with a number of plasticizers indicated good compatibility with TMETN ($CH_3C(CH_2ONO_2)_3$), NEMNC ($O_2NOCH_2CH_2OCON(NO_2)CH_3$) and IDP and incompatibility with BDNPA-BDNPF (1:1) and ADN ($NC(CH_2)_4CN$).

(U) Propellant mixtures were prepared using the candidate binder and the advanced fuels. TMETN, NEMNC or IDP were used as the plasticizers, along with NH_4ClO_4 as the oxidizer. All propellants cured after three days at 135°F. No foaming was observed in the small (0.5 gm) samples.

g. Aziridines and Epoxides (U)

(U) 1-Benzoyl-2-ethylaziridine and 1,2-epoxycyclohexane were compatible with LMH-1, chrome passivated Be and LMH-2 at 50°C for 18 hours (Table LIX).

Table LIX

COMPATIBILITY OF 1-BENZOYL-2-ETHYLAZIRIDINE AND OF 1,2-EPOXYCYCLOHEXANE WITH ADVANCED FUELS (U)

Fuel	Compound Remaining, % after 18 hrs at 50°C: Epoxide	Aziridine
none	49	68
Be	50	68
LMH-1	51	69
LMH-2	49	68

6. Advanced Oxidizers (U)

a. Introduction (U)

(U) The program work statement suggested investigation of the oxidizers, NP, HDP, and HAP with the workhorse binder. Because of difficulties with the first of these oxidizers, the work was limited to the last two with a preponderance of effort on the last. The investigation indicated that HAP may present less difficulty than HDP in preparation of an advanced propellant. Also the incorporation of HAP into a suitable propellant would require solutions to many problems encountered with utilization of HDP.

b. Hydroxy Compounds (U)

(U) Both 1-decanol and 2-octanol were compatible with HAP at 23 and 50°C, but they were not compatible with HDP (Table LX). The nature of the alcohol-HDP reaction was not further investigated.

Table LX

COMPATIBILITY OF 1-DECANOL AND 2-OCTANOL WITH HAP OR HDP AT 23 and 50°C[a] (U)

Oxidizer	Temp °C	Compound Remaining,% $C_{10}H_{21}OH$	Compound Remaining,% $C_8H_{17}OH$
HAP	23	100	100
HAP	50	100	100
HDP	23	78	42
HDP	50	71	27

[a]Oxidizer to alcohol weight ratio of 8 in benzene; after 18 hr.

(U) It was reported that unsaturated alcohols of the allyl type reacted with HAP to form an ether(13). This reaction was investigated.

(U) The compatibility of crotyl alcohol, a model for an allylic alcohol in the workhorse prepolymer or in an unsaturated prepolymer alcohol, was tested with HAP (Figure 62). After 20 hours at 50°C only 6% of the crotyl alcohol remained. A new peak was observed on the chromatogram which had an area equal to 25% of the original area for crotyl alcohol. The unknown compound was formed by contacting crotyl alcohol with HAP at 50°C for 2 weeks and was isolated by preparative gas-chromatography. Infrared analysis indicated that the isolated material was either a cyclic or linear alkene with neither a hydroxy nor an ether function. This task remains to be completed and the successful solution may provide the answer to alcohol incompatibility with HDP.

c. Olefinic Compounds (U)

(U) Olefinic compounds were compatible with both HAP and HDP (Table LXI). While this result appeared inconsistent with reported difficulties in utilization of unsaturated prepolymers with these oxidizers, all of the prepolymers had other functional groups in addition to the olefinic ones. The difficulty might be due to a combination of functional groups rather than to the olefin itself.

d. Carboxy Compounds (U)

(U) The carboxy functional group was completely compatible with both HAP and HDP even at 50°C (Table LXII).

GAS-LIQUID CHROMATOGRAMS OF REACTION MIXTURE OF CROTYL ALCOHOL AND HAP AT 50°C

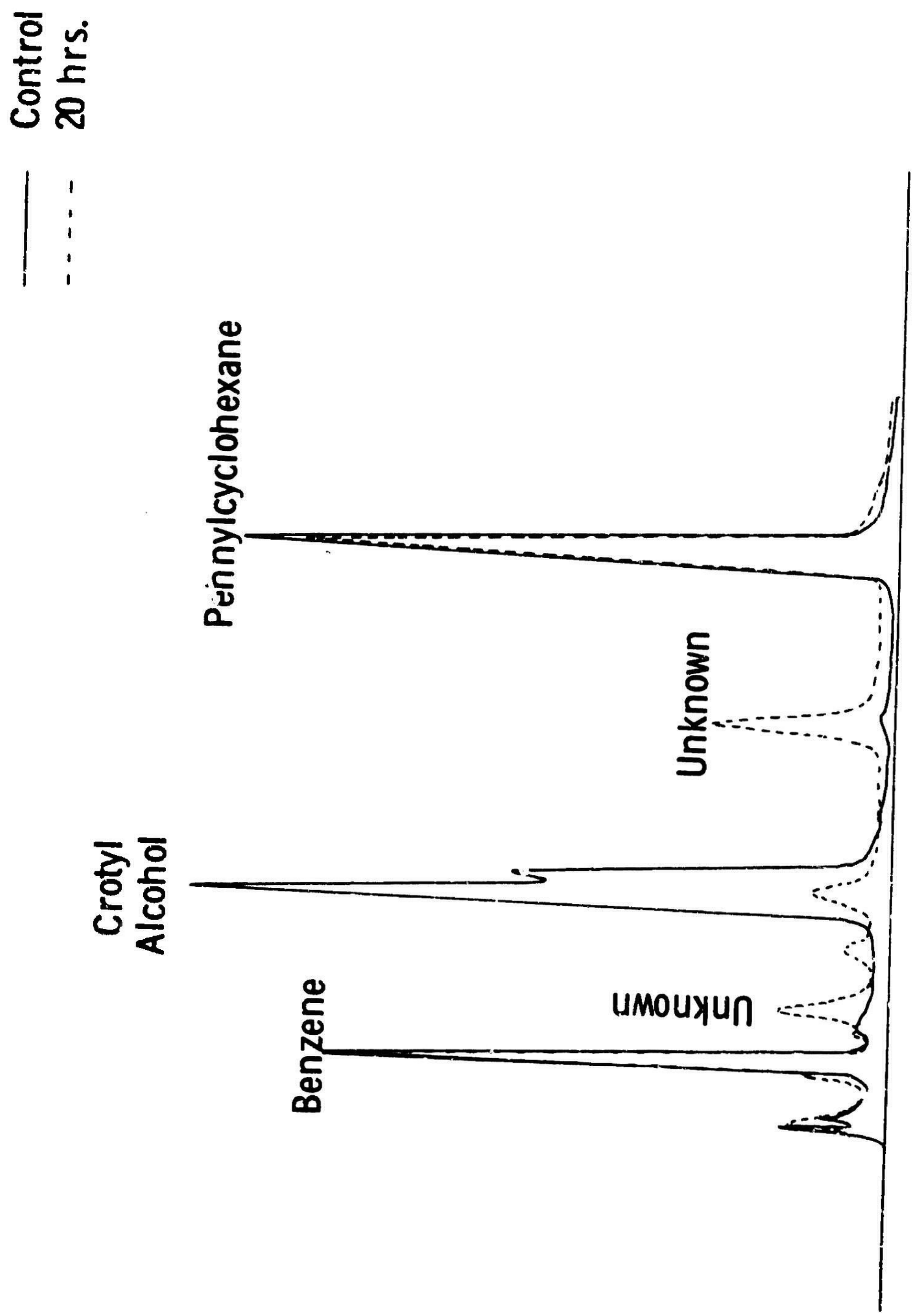


Figure 62

Table LXI

COMPATIBILITY OF 1,7-OCTADIENE WITH HAP AND HDP AT 23 AND 50°C[a] (U)

Oxidizer	Temp °C	Octadiene Remaining, % after 18 hours
HAP	23	97
HAP	50	96
HDP	23	100
HDP	50	100

[a] In benzene; oxidizer to octadiene weight ratio 28.

Table LXII

COMPATIBILITY OF NONANOIC AND 2-ETHYLHEXANOIC ACIDS WITH HAP AND HDP AT 23 AND 50°C[a] (U)

Oxidizer	Temp °C	Acid Remaining, % after 18 hours	
		$C_7H_{15}COOH$	$C_8H_{17}COOH$
HAP	23	100	100
HAP	50	100	100
HDP	23	100	100
HDP	50	100	100

[a] In benzene; oxidizer to acid weight ratio 11.

e. Isocyanate Compounds (U)

(U) The isocyanate compounds reacted with both HAP and HDP (Table LXIII). This interference was not as serious as indicated by the data in Table LXIII because of the factors discussed in the following section.

Table LXIII

COMPATIBILITY OF BUTYL ISOCYANATE WITH HAP AND HDP
AT 23 AND 50°C[a] (U)

Oxidizer	Temp °C	Isocyanate Remaining, % after 18 hours
HAP	23	85
HAP	50	82
HDP	23	33
HDP	50	32

[a] In benzene; oxidizer to isocyanate weight ratio 28.

f. Isocyanate-Alcohol Reaction Systems (U)

(U) While both HAP and HDP consumed isocyanate, the oxidizers were compatible with systems containing both isocyanate and in alcohol. The alcohol was more effective in reacting with the isocyanate than was HAP. The situation was less clear in the case of HDP which was not extensively studied, but the same situation may prevail. Both oxidizers catalyzed the isocyanate-alcohol reactions.

(U) HAP was an excellent catalyst for the formation of urethanes. The reaction of n-butyl isocyanate and 2-octanol at 50°C in the presence of HAP was essentially complete after 4 hours (Table LXIV), whereas the same reaction without HAP was only 15% complete. The isocyanate reaction in the presence of HAP was complete after 150 minutes at a temperature of 23°C indicating that the reaction at 50°C was considerably faster.

(U) The main difference, besides catalysis, in the reaction of isocyanate with alsohol in the presence and absence of HAP was the amount of urethane that was found in solution. In both cases, with and without HAP, the respective consumption of isocyanate and alcohol was approximately equal indicating a stoichiometric reaction. The observation of less urethane than expected for the extent of reaction when HAP was present was caused by adsorption of the urethane on the surface of HAP.

(U) The reaction of n-butyl isocyanate with 2-octanol in the presence of HDP (Figure 63) was considerably faster than the reaction in the presence of HAP (Table LXV). There was also a loss of organic material through a side reaction so that a mass balance was not achieved.

Table LXIV

RATE OF REACTION OF n-BUTYL ISOCYANATE AND 2-OCTANOL IN CONTACT WITH HAP AT 23 AND 50°C[a] (U)

Control (no oxidizer); 50°C

Time, hr	RNCO[b] %	ROH[b] %	Prod[c] %	Σ(ROH + Prod) %
0	100	100	0	100
4	84	86	10	96
8	74	74	21	95
18	51	55	37	92
24	42	44	48	93
48	19	21	72	93
HAP; 50°C				
4	7	9	64	73
8	6	9	60	69
18	5	8	63	71
24	4	12	61	73
48	4	10	60	70
HAP; 23°C				
0	100	100	0	100
0.5	52	52	33	85
1	27	32	52	84
1.5	19	23	52	86
2.5	12	14	58	72
3.5	14	14	59	73
26.8	13	12	50	62

[a] NCO to OH = 1; HAP to substrate ratio = 2.2; in benzene.
[b] % of original remaining.
[c] % of theoretical.

GAS-LIQUID CHROMATOGRAMS OF REACTION MIXTURE OF OCTYL ALCOHOL, BUTYL ISOCYANATE AND HDP AT 23°C

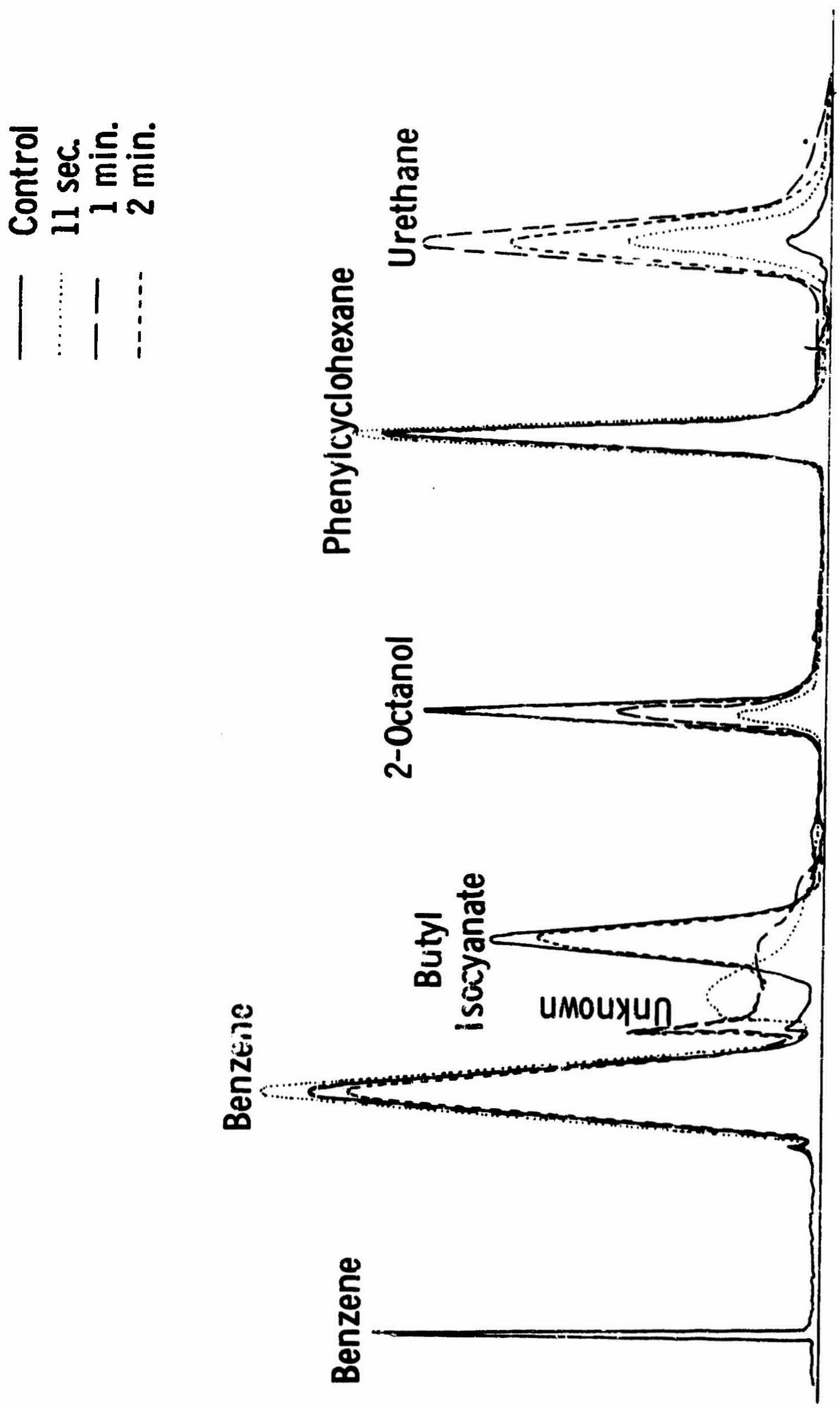


Figure 63

Table LXV

RATE OF REACTION OF n-BUTYL ISOCYANATE WITH 2-OCTANOL IN THE PRESENCE OF HDP AT 23°C[a] (U)

Time, sec	RNCO[b] %	ROH[b] %	Prod %	Σ(ROH + Prod) %
0	100	100	0	100
11	38	46	32	78
60	0	5	62	67
120	0	1	60	61

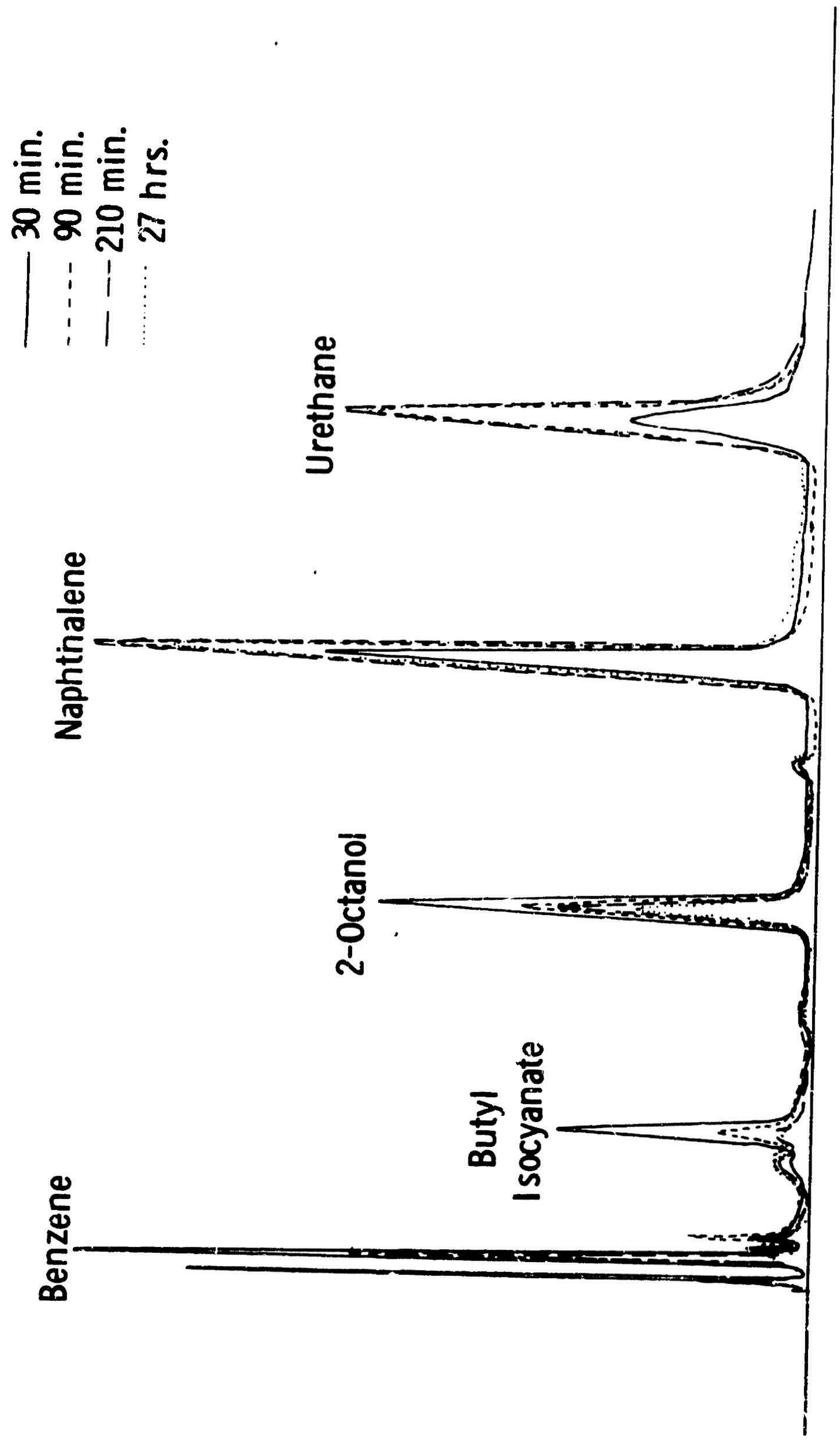
[a] NCO to OH = 1; HDP to substrate ratio = 2.2; in benzene.
[b] % of original remaining.
[c] % of theoretical.

(U) In the reaction of n-butyl isocyanate with 2-octanol in the presence of HAP, even though the reaction was stoichiometric, a quantitative yield of urethane product was not obtained. The stability of the urethane product was determined in the presence of HAP. About 30% of the urethane was adsorbed by or reacted with the HAP in such a way that no new volatile products were formed. This is consistant with the amount of urethane observed from previous rate runs. 2-Octyl N-n-butylcarbamate with HDP formed a two phase benzene solution besides the solid HDP. The upper layer contained about 20% of the carbamate and the lower layer about 40%. Considerable amounts of more volatile compounds were observed by gas chromatography but were not identified. The amount of urethane observed in this test (60%) was quite similar to that shown for complete reaction in Table LXV. Thus the urethane was probably adsorbed on the HAP with little or no chemical interaction. The urethane was similarly adsorbed by the HDP although in this case some side reactions may be occurring. The adsorption of urethane with little or no chemical interaction was further supported by experiments in which the HAP and HDP were dissolved with water and the original amount of urethane added to the solids was recovered.

(C) The reaction of an isocyanate with an alcohol was catalyzed by HAP. Since the catalytic effect of HAP might be due to its acidity, the addition of a base to decrease the acidity might effectively reduce the catalytic effect of HAP. The urethane cure reaction was studied at room temperature in the presence of HAP with (2% by wt) N,N-diallylmelamine (DAM)[14]. The results are given in Table LXVI and a chromatogram of the basic reaction is shown in Figure 64.

(C) The addition of 2% by wt of N,N-diallylmelamine to HAP had only a slight retarding effect on the rate of reaction of isocyanate with

GAS-LIQUID CHROMATOGRAMS OF REACTION MIXTURE OF OCTYL ALCOHOL, BUTYL ISOCYANATE AND HAP AT 23°C



(THIS PAGE IS UNCLASSIFIED)

Figure 64

alcohol. The last column of Table LXVI indicated that a mass balance was not maintained when the reactions were in the presence of HAP. This phenomenon occurred also in the presence of HDP and was explained above. Thus, the use of DAM did not radically change the effect of HAP on the isocyanate-alcohol reaction.

(U) The approach to the preparation of a HAP propellant was based on the observation that side reactions with isocyanate curing agents are minor. The main problem centered about reducing the isocyanate-alcohol rate of reaction. One approach was to use curatives with more hindered or slower isocyanate groups while a second approach sought to retard the reaction rate by the use of solid, insoluble isocyanates. Both approaches were pursued.

Table LXVI

THE REACTION OF n-BUTYL ISOCYANATE WITH 2-OCTANOL IN THE PRESENCE OF HAP AND N,N-DIALLYLMELAMINE AT ROOM TEMPERATURE[a] (C)

	Time, hrs	Constituent, %			
		RNCO[b]	ROH[b]	RNHCOOR[b]	ROH + RNHCOOR
A. No additives	2	100	96	2	98
	20	90	89	8	97
B. HAP present	0.5	52	52	33	85
	1.0	27	32	52	84
(C)	24.0	13	12	50	62
C. DAM present	2	97	97	2	99
	20	84	85	11	96
D. AP + DAM present	0.5	19	30	48	78
	1.0	13	22	53	75
	20.0	7	18	58	76

[a]NCO to OH = 1; oxidizer to substrates ratio = 2.2; in benzene.
[b]% of original remaining.
[c]% of theoretical.

(U) The use of the solid, insoluble diisocyanates, Carwinate 136T (bitolylene diisocyanate, Upjohn Co.) and Nacconate H-12 (4,4'-methylene bis[cyclohexyl isocyanate], Allied Chemical, National Aniline Division) as a substitute for CTI and HDI with GTRO as a trifunctional crosslinking agent was not successful. The propellants did not cure even at 50°C. Rate retardations by the use of hindered isocyanates have not been investigated yet.

g. Aziridines and Epoxide Compounds (U)

(U) Solutions of the various model compounds were added to

the solid fuel, oxidizer or mixture of the two and periodically analyzed by gas chromatography for concentration changes.

(U) 1-Benzoyl-2-ethylaziridine and 1,2 epoxycyclohexane were incompatible with HAP at 23° for 18 hours (Table LXVII). The reaction of the aziridine and epoxide with an appropriate carboxylic acid was very slow at 23°; thus, the loss of both compounds was probably due to a HAP catalyzed homo-polymerization (Table LXVIII). Very little reaction with the acid occurred at either temperature.

Table LXVII

COMPATIBILITY OF 1,2-EPOXYCYCLOHEXANE AND OF 1-BENZOYL-2-ETHYLAZIRIDINE WITH HAP AND HDP AT 23° AND 50°C (U)

Oxidizer	Temp °C	Epoxide[a] %	Aziridine[a] %
HAP	23	-	31[b]
HAP	50	0	12[c]
HDP	23	16	24
HDP	50	9	0

[a] % of original remaining after 18 hr.
[b] 29% oxazolines also present.
[c] 21% oxazolines also present.

Table LXVIII

COMPATIBILITY OF 1,2-EPOXYCYCLOHEXANE + HEXANOIC ACID AND 1-BENZOYL-2-ETHYLAZIRIDINE + PROPIONIC ACID WITH HAP[a] (U)

	Temp, °C	Aziridine %	Propionic Acid, %	Epoxide %	Hexanoic Acid, %
Control	23	58.4	39.8	35.6	59.8
	50	-	-	33.0	59.5
HAP	23	0[b]	36.2	27.5	59.8
	50	-	-	3.6	56.5

[a] Percents remaining; based on use of internal standard.
[b] 13.6% 2-Phenyl-4-ethyloxazoline present.

(U) A search was made to find an effective catalyst for the epoxide-carboxylic acid reaction so that the curing agent would be more effective. A number of catalysts were tested in the system 1,2-epoxycyclohexane-hexanoic acid at the 2% by weight level. The reactions were run in benzene at 50°C for 18 hours and the products and reactants analyzed by gas chromatography. COT (Aerojet Proprietary), COT plus triethanolamine and the Schiff base of n-butylamine and salicylaldehyde were twice as effective as the chromic trichloride complex of triethanolamine and FeAA. The copper and cobalt salts of linoleic and stearic acid, the chromium complex of β-hydroxyquinoline, dibutyltin dilaurate, N,N-dibenzylamine, quinoline and pyridine were ineffective as catalysts for the epoxy-acid reaction. None of the catalysts were effective enough to hold promise for epoxide-cured HAP propellants.

h. Effect of Crystalline Solids on Aziridines (U)

1) Effect of Reactive Solids on Curing Agents (U)

(U) A general problem common to advanced propellants has been the tendency of the crystalline solids to rearrange, polymerize or react with the curing agents. It has been postulated that the acidity of the solids is the chief cause of these reactions, but the postulate has never been tested.

(U) Experiments were performed with 1-benzoyl-2-ethylaziridine which is prone to both rearrangement and polymerization and a series of potassium and ammonium salts to shed light on the factors which were responsible. The salts included potassium and ammonium perchlorates, sulfates, nitrates, borofluorates, chlorides, bromides and iodides.

2) Rearrangement of Aziridines (U)

(U) The only potassium salts that promoted rearrangement were the bromide and iodide, whereas all the ammonium salts catalyzed the rearrangement of the aziridine to some extent. The potassium salts were more discriminatory as to which oxazoline isomer was formed; the 4-ethyl-1-phenyloxazoline-2 (80%) predominating. The ammonium nitrate and perchlorate produced mainly the 5-ethyl-1-phenyloxazoline-2 (82%) while the halogens produced a 50:50 mixture of the 4- and 5-ethyl-1-phenyloxazoline-2.

(U) The salts that were examined as promoters of the rearrangement of benzoyl-2-ethylaziridine to its oxazoline isomers showed varying degrees of rearrangement with time. Of the two series of salts that were used, the ammonium salts caused rearrangement to occur more rapidly than the corresponding potassium salts. For the ammonium salts the rate of rearrangement decreased in the order iodide > bromide, nitrate >> perchlorate > chloride, borofluorate > sulfate, while only the potassium iodide and bromide affected rearrangement of the aziridine over the time period studied. The order was iodide > bromide.

3) Polymerization of Aziridine (U)

(U) Besides rearrangement, benzoyl-2-ethylaziridine can undergo homopolymerization. The amount of polymer (~15%) formed in the

presence of all the salts except ammonium perchlorate and nitrate is essentially equal to that which would be formed if the aziridine were heated for a specific length of time without the salts being present. In the presence of ammonium perchlorate and ammonium nitrate, benzoyl-2-ethylaziridine yielded 46 and 25% polymer, respectively.

4) Significance of the Results (U)

(U) The rearrangement of 1-benzoyl-2-ethylaziridine to 4-ethyl or 5-ethyl-1-phenyloxazoline-2 can occur by either a homogeneous path, i.e., the reaction of the aziridine with dissolved salt, or by a heterogeneous path. The bromides and iodides were shown to be dissolved to a small extent in the reaction solution since a silver halide precipitate formed in an aqueous silver nitrate extract of the reaction solution. The fact that the rearrangement of the aziridine occurs by both paths was further substantiated by the rearrangement of the aziridine with 0.1 g and 0.001 g of ammonium iodide. In both cases, solid ammonium iodide was observed in the reaction flask. The data in Table LXIX indicates that the homogeneous reaction, which should be a large fraction of the 0.001 g NH_4I sample, is much slower and produces mainly the 4-substituted isomer. The presence of considerably more solid (0.1 g NH_4I sample) increases the rate of rearrangement but also increases the amount of 5-ethyl-1-phenyloxazoline-2 such that the latter tends to be approximately 50% of the products formed.

Table LXIX

HOMOGENEOUS AND HETEROGENEOUS REARRANGEMENT OF 1-BENZOYL-2-ETHYLAZIRIDINE ON NH_4I (U)

		Composition, %		
		Oxazoline		
NH_4I, g	Time, hr	4-ethyl	5-ethyl	Aziridine
0.1	1	36	29	35
	3	49	51	0
	5	49	51	0
	23	52	48	0
0.001	1	21		79
	3	43		57
	5	65		35
	23	69	31	-

(U) The formation of the two products varied with the particular salt used. The potassium halides favored formation of 4-ethyl-1-phenyloxazoline-2 while the replacement of potassium with ammonium affected partial rearrangement to the 5-ethyl-1-phenyloxazoline-2 isomer.

(U) It thus seems reasonable that the rearrangement of 1-benzoyl-2-ethylaziridine to 5-ethyl or 4-ethyl-1-phenyloxazoline-2 in the

presence of various solid inorganic salts can occur via a homogeneous or heterogeneous path with the two paths not necessarily giving the same products or ratio of products. The differences noted with the various ammonium salts indicated that while the acidity of the salt was important, it was not the sole factor.

i. Heteroazolines (U)

(U) In the search for new curing agents for advanced oxidizers the reactions of a number of heteroazolines with propionic acid in the presence of HAP were studied. The reactions, carried out at room temperature, included the compounds, 2-phenyl-4-ethyloxazoline-2, 2-phenyl-5-ethyloxazoline-2, 2-ethyloxazoline-2, 2-ethylthiazoline-2, and 2-methylimidazoline-2. All the compounds were incompatible with HAP. No amide-ester product was formed, after 24 hr at 23°C, and all the compounds were completely consumed by side reactions. The side reactions of the various heteroazolines with HAP were not determined.

7. Advanced Fuels - Advanced Oxidizer Systems (U)

a. Isocyanate-Alcohol (U)

(U) The combinations of an advanced fuel and HAP decreased the rate of the isocyanate-alcohol reaction. As a result there was an increased loss of isocyanate to side reactions and a considerable decrease in the detectable amount of urethane product (Tables LXX and LXXI). The reactions were still fast, especially at 50°C and became more non-stoichiometric.

Table LXX

RATE OF REACTION OF n-BUTYL ISOCYANATE AND 2-OCTANOL WITH HAP OR WITH HAP AND Be AT 50°C[a] (U)

Time, hr	RNCO[c] %	ROH[c] %	Urethane[d] %	Σ(ROH + Urethane) %
		HAP[b]		
4	7	9	64	73
8	6	9	60	69
18	5	9	63	71
24	4	8	61	73
48	4	12	60	70
		HAP-Be (1:1)[e]		
4	4	15	56	71
8	5	20	44	64
18	4	23	47	69
24	-	18	37	55
48	-	18	34	52

[a]NCO to OH = 1:1 equivalent ratio; for control see Table LXIV.
[b]Solids to component ratio is 2.2:1. [c]% of original remaining.
[d]% of theoretical. [e]Solids to component ratio is 1:1.

Table LXXI

RATE OF REACTION OF n-BUTYL ISOCYANATE AND 2-OCTANOL WITH HAP AND WITH HAP AND Be OR LMH-2 AT 23°C[a] (U)

HAP[b]

Time, min	R-NCO[c] %	R-OH[c] %	Urethane[d] %	Σ(ROH+Urethane) %
0	100	100	0	100
30	52	52	33	85
60	27	32	52	84
90	19	23	52	86
150	12	14	58	72
210	14	14	59	73
1610	13	12	50	62
		HAP-Be (1:1)[e]		
30	77	80	16	96
60	60	72	35	107
90	32	32	46	78
150	14	21	47	68
210	26	27	44	71
1610	21	32	40	72
		HAP-LMH-2 (1:1)[e]		
30	72	79	8	87
60	52	70	15	85
90	50	65	17	82
150	27	43	20	53
210	15	37	20	57
1610	13	31	17	48

[a]NCO to OH = 1:1 equivalent ratio.
[b]Solid to component weight ratio is 2.2:1.
[c]% of original remaining.
[d]% of theoretical.
[e]Solid to component weight ratio is 1:1.

(U) The reaction of n-butyl isocyanate and 2-octanol in the presence of treated LMH-1 and HAP with and without catalysts T-12 and T-20 gave similar results. The catalytic effect of HAP controls the rate of the isocyanate-alcohol reaction and the amount of urethane formed in all cases is identical to that found earlier when the reaction is carried out only in the presence of HAP (Table LXXII).

Table LXXII

CATALYZED REACTION OF n-BUTYL ISOCYANATE WITH 2-OCTANOL IN THE PRESENCE OF LMH-1 (TREATED), AND HAP AT 25°C[a] (U)

Catalyst	Time, hr	C_4H_9NCO[b]	$C_8H_{17}OH$[b]	Urethane[c]	Total Alcohol + Urethane
None	0.25	76.0	72.0	20.3	92.3
	0.50	38.3	41.2	41.3	82.5
	0.75	37.5	38.4	45.6	84.0
	1.00	14.5	18.4	63.0	81.4
	1.50	8.9	12.0	66.5	78.5
	3.50	6.7	11.1	64.8	75.9
	24.00	4.1	10.3	68.5	78.8
T-12	0.25	61.3	60.7	29.0	89.7
	0.50	42.0	40.3	44.5	84.8
	0.75	22.6	22.7	56.3	79.0
	1.00	21.6	18.5	58.5	77.0
	1.50	10.9	11.5	70.6	81.6
	2.00	7.5	9.3	70.2	79.5
	4.50	5.7	8.7	68.4	77.1
	23.00	4.4	7.3	70.8	78.1
T-20	0.25	60.2	51.2	36.3	87.5
	0.50	35.7	32.0	51.3	83.3
	0.75	14.8	14.4	55.6	70.0
	1.00	16.7	12.8	68.1	80.9
	1.50	8.1	9.1	69.0	78.1
	3.75	2.9	8.6	69.3	77.9
	24.00	4.3	8.5	66.5	75.0

[a] Binder to HAP wt ratio 4:1 and 0.1% catalyst based on binder weight.
[b] Percent of original.
[c] Percent of theoretical.

(U) Although adsorption of the urethane by the HAP reduced the urethane to about 80% of theoretical, the results were encouraging, considering the highly reactive ingredients. The major difficulty continued to be the very rapid isocyanate-alcohol reaction in the presence of HAP.

b. 1,2-Epoxycyclohexane (U)

(U) After 18 hours at 50°C in contact with mixtures of HAP and Be or LMH-2, no epoxycyclohexane could be detected.

8. Advanced Propellants (U)

(U) Propellants with NH_4ClO_4 and each of the advanced fuels were prepared on a 400-gram scale and stored for aging studies. The composition of these propellants are shown in Table LXXIII.

Table LXXIII

ADVANCED PROPELLANT FORMULATIONS FOR AGING STUDY (U)

(C)

Component	Composition, Wt.		
NH_4ClO_4	64.00	72.00	69.00
AlH_3	16.00	-	-
Be	-	14.00	-
BeH_2	-	-	12.00
Telagen S	13.90	9.67	12.12
CTI	0.24	0.23	0.32
HDI	0.85	0.60	0.81
IDP	5.00	3.50	4.75
T-20	0.01	-	-

(U) Attempts have been made at incorporating HAP into a work-horse binder propellant, but none has been successful. One such attempt was made with the propellant shown in Table LXXIV.

Table LXXIV

HAP Propellant (U)

(C)

	Wt%
Telagen S	10.43
CTI	.18
HDI	.64
IDP	3.75
Al	15.00
HAP	70.00

(U) However, this propellant had an extremely short potlife and could not be cast. A sample of this propellant showed a hard cure after standing overnight at ambient conditions, but the physical properties were poor.

(U) The very high cure rate of the above formulation led to the use of other isocyanates to slow down the rate of cure and thereby extend the potlife. Two isocyanates, Carwinate 136T and Nacconate H-12, were tried.

(U) Carwinate 136T is a yellow crystalline solid. It was not suitable because it was insoluble in the binder. Nacconate H-12 was more promising than 136T, although the first propellants made with it did not cure. Work is continuing with this isocyanate.

9. Complex Hydroxylamine Perchlorate (U)

(C) Workers at Aerojet under another program (Contract NOw 66-0463-C) were studying the stabilizing effect of amines on hydroxylamine perchlorate propellants and reported the use of DAM in these propellants[14]. Other workers (Contract DA-01-021-AMC-12110 (Z)) observed that when the amine was added to a solution of HAP, a crystalline solid was precipitated[15]. The solid was tentatively identified as HAP which it resembled by differential thermal analysis. More important, the solid was not hygroscopic.

(C) Investigations of the material on this program showed that the amines that reacted with HAP had a pKa between 8 and 10. Typical bases used were aniline, phenylhydrazine, N,N-dimethylaniline, quinoline, and DAM. The HAP obtained from the reaction of an amine with HAP contained either one or two extra moles of hydroxylamine depending upon the initial concentrations of the reactants. The extra hydroxylamines were probably bound to the hydroxylamine perchlorate in a similar manner as water is bound to a hydrated salt. The complexes were designated HAP-X and HAP-2X.

(U) The molecular composition of the white solids prepared by the reaction of HAP with an appropriate base, was confirmed by reacting HAP with hydroxylamine. The equivalent weights of the compounds were determined by titration for the amount of perchlorate using standard base and the amount of hydroxylamine using perchloric-acetic acid. The titration data are given in Table LXXV.

Table LXXV

EQUIVALENT WEIGHT OF HAP COMPLEXES BY TITRATION (U)

	With Base		With Acid	
	Found	Theory	Found	Theory
HAP	133	133.5	-	-
HAP-X[a]	166	166.5	165	166.5
HAP-2X[b]	200	199.6	100	99.7

[a] From reaction of 1 eq. HAP with 1 eq. of NH_2OH.
[b] From reaction of 1 eq. HAP with 2 eq. of NH_2OH.

(U) An elemental analysis of HAP•X is shown in Table LXXVI. The analysis for HAP•2X gave essentially the same values for the monocomplex. The reason for this is not known, but the compound may have decomposed to the monocomplex under the conditions of the analysis.

Table LXXVI

ELEMENTAL ANALYSIS OF HAP-X (U)

Element	Analysis, % Found	Analysis, % Theory
Cl	21.2	21.2
H	4.77	4.22
N	17.6	16.8

(U) The differential thermal analysis of the complex hydroxylamine perchlorates differed sufficiently to allow distinguishing between the three forms. The DTA data are given in Table LXXVII and in Figures 65-67.

Table LXXVII

DTA[a] OF COMPLEX HYDROXYLAMINE PERCHLORATES (U)

	Endotherm, °C	Exotherm, °C[b]
HAP	55, 88	190
HAP-X	75, 100	110
HAP-2X	80	110

[a]Heating rate 0°/min in air.
[b]Start of exotherm.

(U) Figure 65 is the thermogram of HAP obtained from Thiokol Chemical Corporation (Lot 85365027) and Figures 67 and 68 are the thermograms for the mono- and di-hydroxylamine complex. The double endotherms exhibited by HAP at 55° and 88°C are present in the thermogram for HAP-X at 75° and 100°C. The HAP-2X showed only one endotherm. The thermograms were good identifications of the complex present.

(U) The melting point of the monocomplex was established by microscopic studies to be 84-82°C. Both complexes were decomposed on melting. They gassed and were converted to NH_4ClO_4; the stoichiometry of this conversion was not established.

DIFFERENTIAL THERMAL ANALYSIS OF HAP
(Air; 10°C/min, Glass Beads) (U)

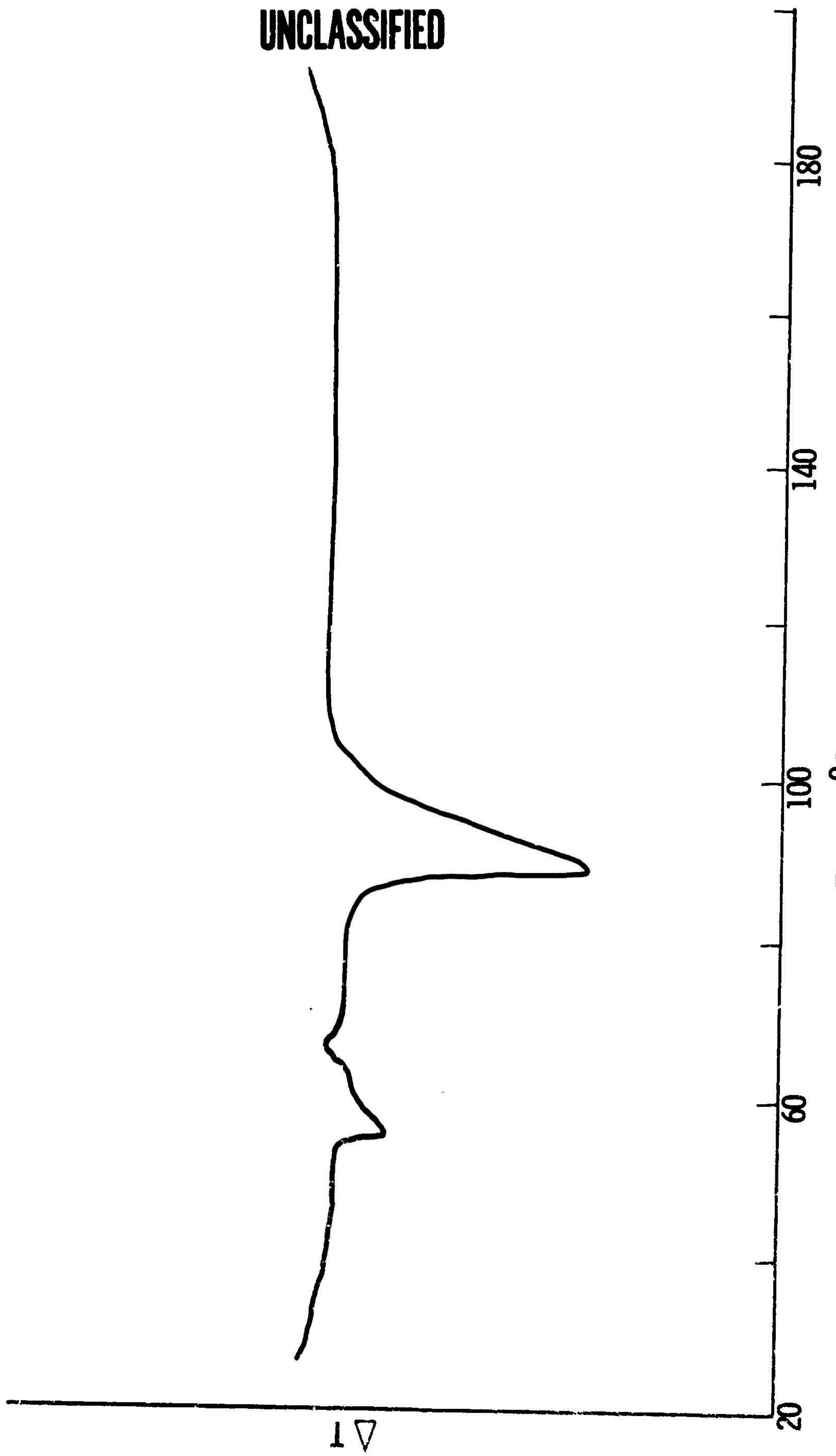


Figure 65

DIFFERENTIAL THERMAL ANALYSIS OF HAP· X
(Air; 10^{0}C/min; Glass Beads) (U)

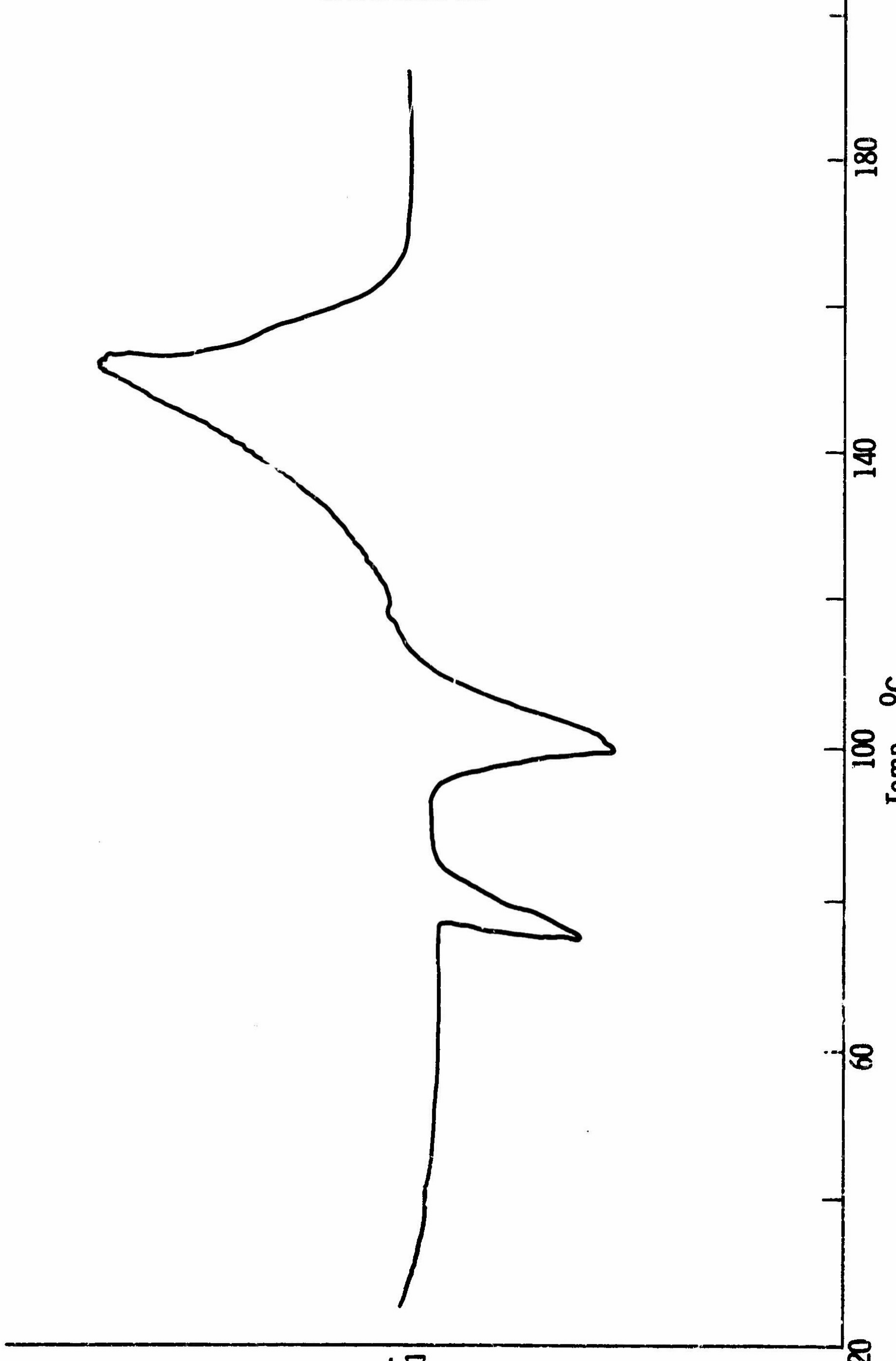


Figure 66

DIFFERENTIAL THERMAL ANALYSIS OF HAP · 2X
(Air; 10^{0}C/min; Glass Beads) (U)

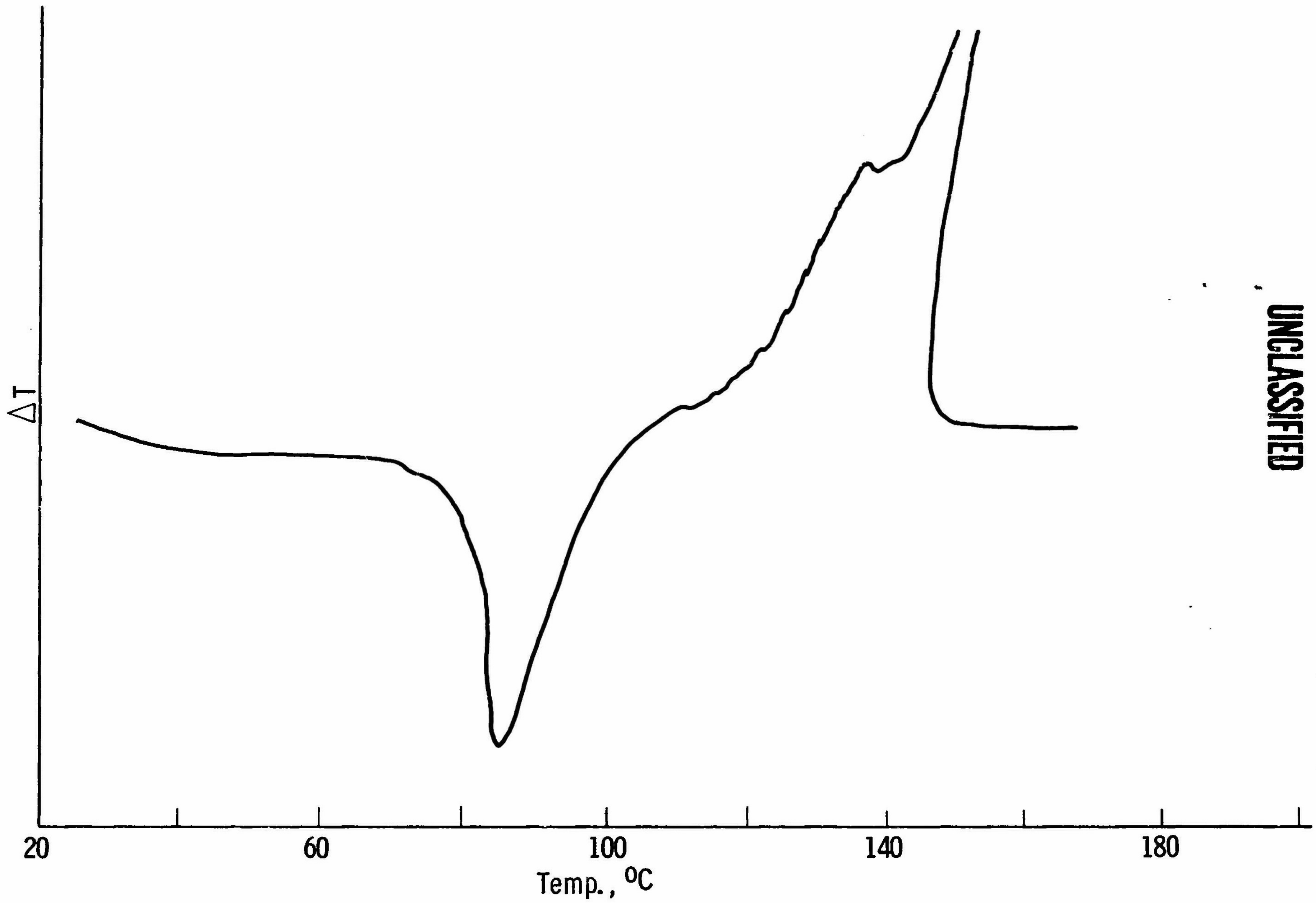


Figure 67

PHOTOMICROGRAPHS OF HAP-X (U)

Under single and double polarized light. Bright spots indicate impurities.

Block-like crystals

Figure 68

(U) The density of HAP-X was 1.97 when prepared from HAP by the addition of DAM and 1.93 when prepared by addition of NH_2OH to HAP. Some photomicrographs of the materials were made (Figure 68).

(U) The hygroscopicity of the three hydroxylamine perchlorates was determined. Weighed samples were allowed to stand under atmospheric conditions for 60 hours. The HAP gained 11.7% in weight whereas the complex HAP compounds showed no increase in weight.

(U) Work on the previously mentioned program[16] indicated that the complexes were compatible with TVOPA, NFPA, BDNPA and BDNPF, LMH-1 and LMH-2.

10. Theoretical Specific Impulse for HAP (U)

(U) In preparation for compatibility studies with HAP, thermodynamic calculations were made for the systems involving this oxidizer with aluminum and the workhorse binder. The results in Figures 69-72 include similar calculations for the analogous unsaturated binder.

(U) The unsaturated analogue shows an expected advantage in theoretical impulse because of the higher heat of formation of the unsaturated binder (-7.848 kcal/100g compared to -46.9615 kcal/100g for the saturated binder).

(U) For systems utilizing the workhorse binder, the HAP to binder ratio of interest would be about 7:1.

D. PHASE THREE (U)

(U) Phase Three involved the synthesis and investigation of curing agents on an "as needed" basis. The results of the work done in this phase have been reported in Sections B and C. The work included preparation of CTI, model curing agents such as 1-benzoyl-2-ethylaziridine, and some work on complex hydroxylamine perchlorates.

E. PHASE FOUR (U)

1. Introduction (U)

(U) Phase Four involved the determination of the environmental stability of Phase One propellants over an extended period. Phase Two propellants were also aged during this phase. In addition, a Phase One propellant was cycled to failure in an analogue cylindrically perforated grain.

2. Conventional Propellants (U)

(U) Propellants (compositions shown in Table XXX) were cut and prepared for an extended aging study. The aging conditions are shown in Figure 73. Both exposed and aluminum wrapped blocks of propellant were used. The Minuteman Wing VI Second Stage Propellant served as a control.

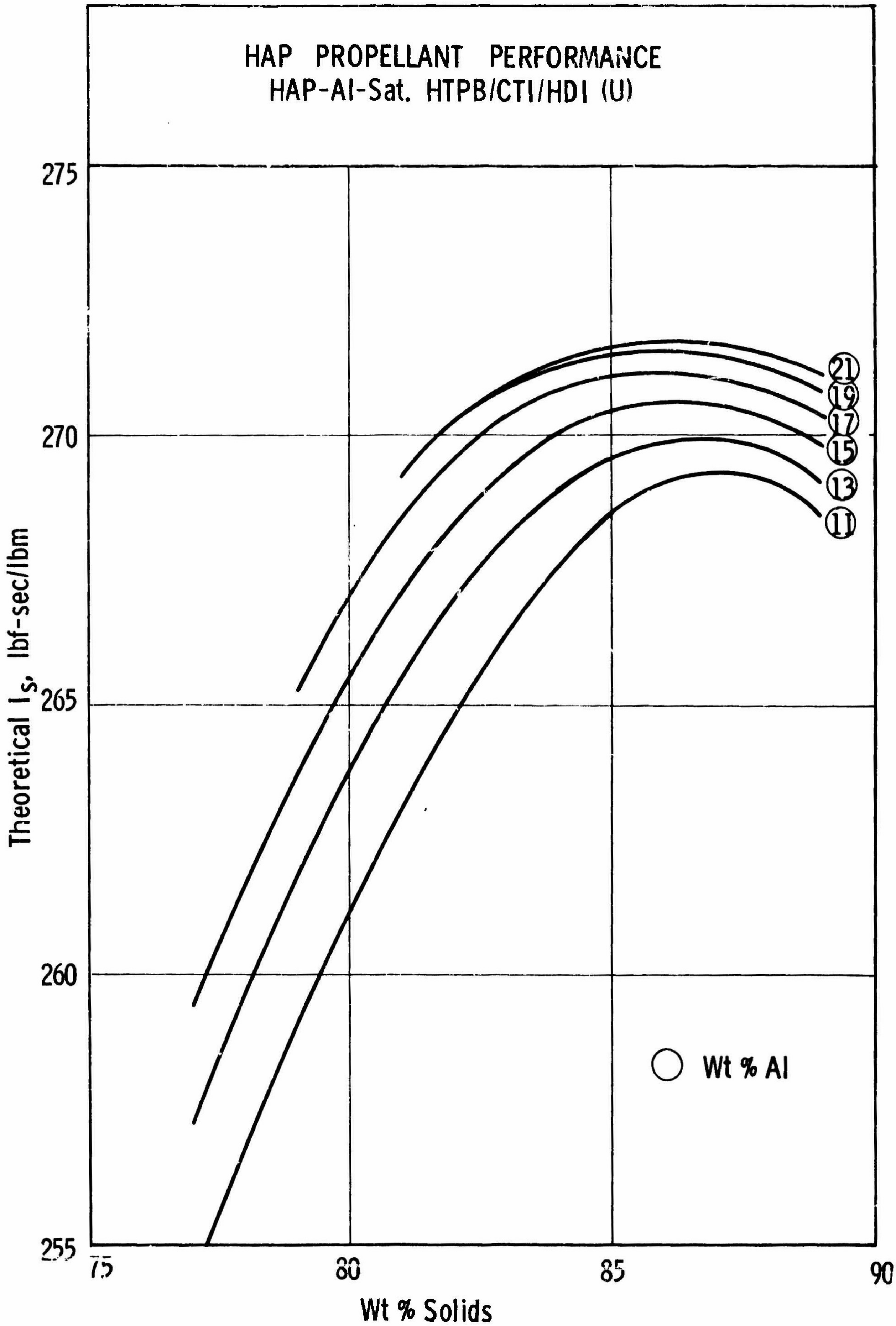
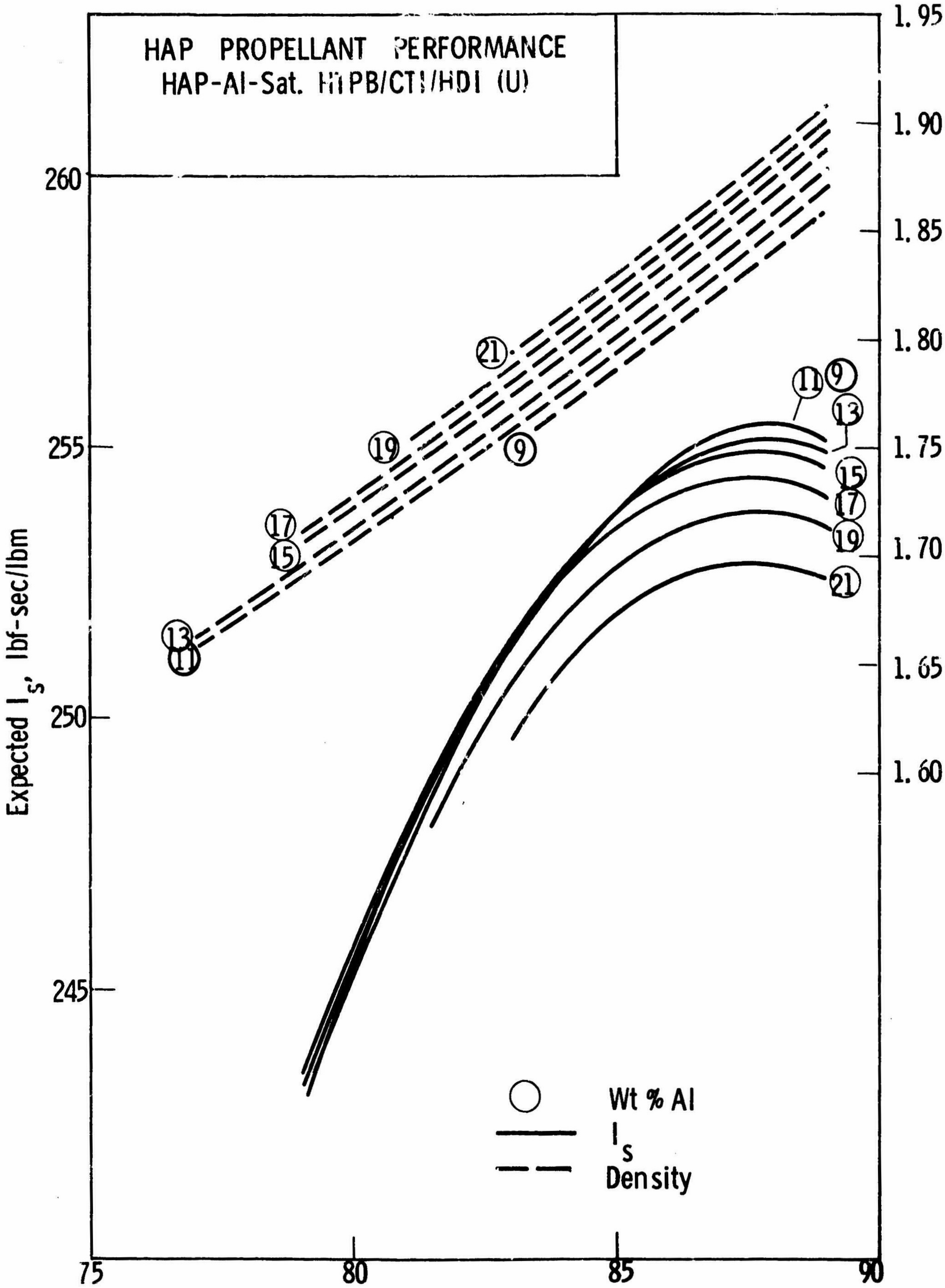

HAP PROPELLANT PERFORMANCE
HAP-Al-Sat. HTPB/CTI/HDI (U)
275
270
265
260
255
75
80
85
90
Theoretical I_s, lbf-sec/lbm
Wt % Solids
21
19
17
15
13
11
Wt % Al

Figure 69



HAP PROPELLANT PERFORMANCE
HAP-Al-Sat. HTPB/CTI/HDI (U)
260
255
250
245
1.95
1.90
1.85
1.80
1.75
1.70
1.65
1.60
Expected I_s, lbf-sec/lbm
Density, gm/cc
21
19
17
15
13
11
9
Wt % Al
I_s
Density
75
80
85
90
Wt % Solids

Figure 70

THEORETICAL SPECIFIC IMPULSES FOR HAP-Al-HTPB/CTI/HDI PROPELLANTS AT VARIOUS Al CONTENTS AND SOLIDS LOADINGS (U)

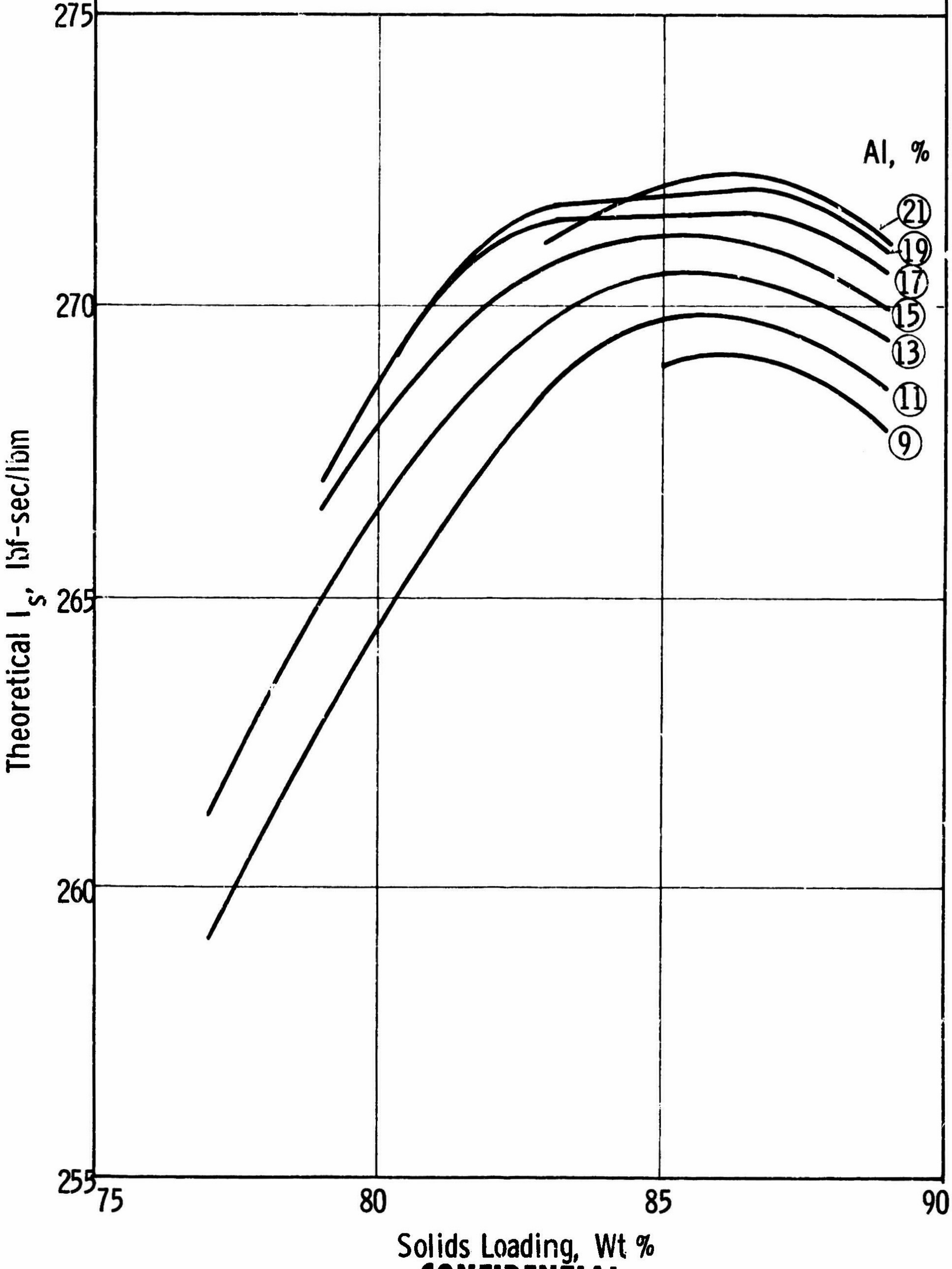


Figure 71

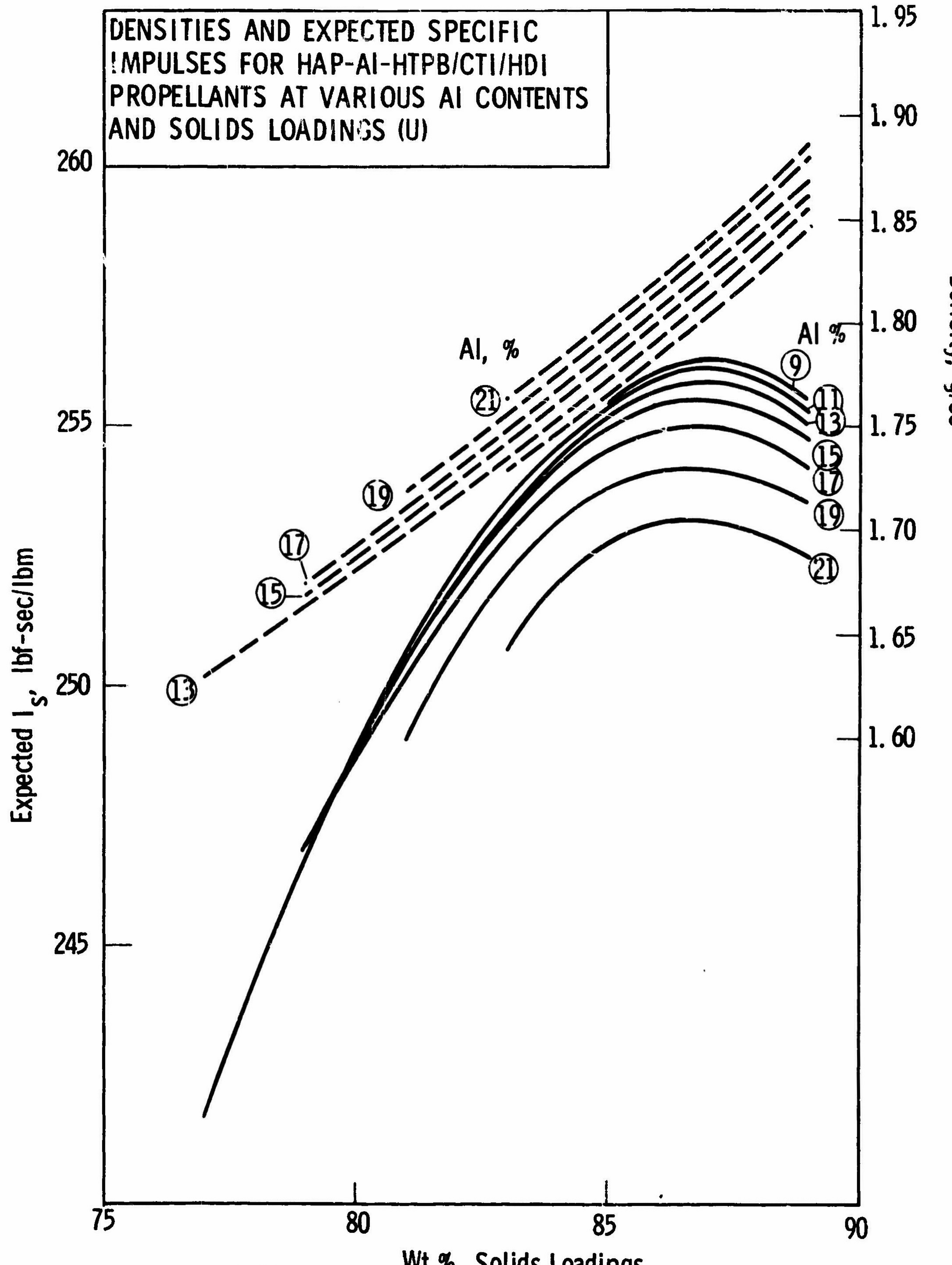

DENSITIES AND EXPECTED SPECIFIC IMPULSES FOR HAP-Al-HTPB/CTI/HDI PROPELLANTS AT VARIOUS Al CONTENTS AND SOLIDS LOADINGS (U)
Expected I_s, lbf-sec/lbm
260
255
250
245
Density, g/cc
1.95
1.90
1.85
1.80
1.75
1.70
1.65
1.60
Al, %
21
19
17
15
13
Al %
9
11
13
15
17
19
21
75
80
85
90
Wt %, Solids Loadings

Figure 72

ENVIRONMENTAL CONDITIONS FOR STUDYING AGING OF CONVENTIONAL PROPELLANTS

HUMIDITY, %	TEMPERATURE, ^{o}F -75	0	77	160 - 170
100	I (CO_2)	I (CO_2)		
80			S	S
50			C I (A)	
25 - 30			C	C
5			I (A)	

S = Stagnant Air C = Circulating Air I = Inert (N_2, CO_2 or A)

Figure 73

(U) The first of these propellants has been aged for 3½ months and several samplings have been made. The testing was delayed by difficulties with the propellant cutting facilities. These difficulties have been overcome and testing is in progress. The test results will be included in subsequent reports.

(U) An analogue cylindrically perforated grain was cycled to failure. The results of this test are reported in Section IV.B.7.i..

3. Aging of Advanced Propellants (U)

(U) Propellants incorporating the various advanced fuels (Table LXXIII) were mixed and cured. Samples of the batches containing Be and LMH-2 were stored under controlled humidity at 80°F (27°C) for aging. One sample of each propellant was placed in a sealed container at a relative humidity of 30%. A second sample of each propellant was placed in a sealed container with Drierite at a very low relative humidity. Neither propellant has shown any change of appearance or of hardness after 4½ months. The aging will continue.

(U) The propellant containing LMH-1 has just begun a similar aging program. No test data are available, but will be reported in subsequent reports.

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4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

FINAL REPORT - 14 March 1966 to 13 March 1967

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13. ABSTRACT

(U) The investigation and characterization of the saturated hydrocarbon binder developed under Contract AF 04(611)-10386 for use in solid rocket propellants were continued. The molecular weight and functionality distributions were determined for the saturated hydrocarbon prepolymer and found to be independent of each other. Analytical data were obtained for saturated and unsaturated prepolymers with hydroxy or carboxy terminal groups.

(U) While NH_4ClO_4 and Al were compatible with the isocyanate curing agents, many plasticizers were not. Of the plasticizers, the hydrocarbon oils were most compatible. The difficulties with the plasticizers were the presence of impurities and an effect (not the result of impurities) on the cure of binders. Binders were made from the Telagen S prepolymers and characterized by uniaxial tensile behavior at 77°F, stress relaxation at 77° and 150°, compression after swelling in toluene, gel and sol fractions, and Mooney-Rivlin constants. Linear relations were demonstrated between the gel fraction, the Mooney-Rivlin C_1 constant, the crosslink density, and the logarithm of the initial uniaxial tensile modulus and of the maximum tensile stress. These data obtained for binders containing a variety of plasticizers seemed to indicate that no plasticizing action exists in these binders. Swelling studies in a large number of solvents indicated a CED value of about 80 for the binder. Two new curing agents, RTDI (an isocyanate) and C-100 (an aziridine), were inferior to the currently used CTI-HDI combination. Propellant studies led

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Saturated Hydroxy Terminated Polybutadienes Saturated Carboxy Terminated Polybutadienes Telagen S Effect of Plasticizers on Mechanical Behavior of Telagen S Binders and Propellants Viscosity of NH_4ClO_4-Oronite-6 Slurries High Solids Propellant Beryllium LMH-1 LMH-2 HAP HDP Compatibility of Advanced Oxidizers with Saturated Hydrocarbon Prepolymers Hydroxylamine Complexes of Hydroxylamine Perchlorate						

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13. ABSTRACT (Cont)

to a candidate formulation which differed slightly from the original workhorse propellant. This propellant showed good aging in screening tests, but continued to have disappointing properties at low temperature. Two 125-lb batches of the propellant were prepared, cast, cured, and placed in long-range aging.

(C) The pressure exponent for burning rate was 0.7 for these propellants (88 wt% solids). The relative viscosity of NH_4ClO_4-Oronite 6 slurries was at a minimum for an oxidizer blend of 35.80%, 32.10% and 32.10% by weight of particles averaging 6, 148, and 419μ, respectively. This blend was used to prepare a high solids loaded propellant with 79% NH_4ClO_4, 12% aluminum, and 9% Telagen S binder at 60-lb scale. Small motors of this propellant, which had a burning rate-pressure exponent of about 0.8, were fired. The specific impulse at standard conditions for large motors was 250 lbf-sec/lbm. The mechanical behavior of this propellant was extensively characterized.

(U) The compatibility of the prepolymer and model compounds with beryllium, LMH-1 and LMH-2 was determined. The most difficulty involved LMH-1 and a model isocyanate. Propellants were made with the Be and LMH-2, but preparation of propellants with LMH-1 required pretreatment of the LMH-1 and catalysis of the isocyanate reaction to maintain ambient curing conditions.

(C) Compatibility studies were extended to include epoxide and aziridine curing agents as well as isocyanates and the oxidizers HAP and HDP. Carboxy, hydroxy,

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and olefinic functional groups were compatible with HAP. Isocyanate was the only curing agent which appeared practical in the HAP system. Both HAP and HDP accelerate the isocyanate-alcohol reaction. In the case of HAP, the use of the amine DAM slowed the isocyanate reaction although it was still much faster than in the absence of the HAP. Both of the oxidizers, physically adsorbed urethane, but with HDP, some chemical degradation was also observed. A series of hydroxylamine-HAP complexes were made, identified, and studied.

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